

Solid-Phase Extraction of Phenolic Compounds with Poly[Metalloprotoporphyrin IX]

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ABSTRACT: A highly insoluble metalloporphyrin polymeric material was used as sorbent for the solid-phase extraction of phenolic compounds. Substantial quantities of phenols (40 to 60 mg/g polymer) were absorbed from aqueous solution comparing satisfactorily with other extraction methods. The polymeric phase presented similar K_{SPE} values for the hydrophobic compounds tested such as *p*-chlorophenol, BPA, *p*-nitrophenol, and a significant lower value for the more hydrophilic *p*-aminophenol and cresol. Several metallic complexes of protoporphyrin IX (Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Fe^{3+}) have been tested. The analytes were extracted with high recoveries at acid and neutral pH values, whereas at pH 10 low recoveries were obtained. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3038–3043, 2001

Key words: metalloporphyrin; polymer; sorbent; solid phase extraction; phenolic compounds

INTRODUCTION

Phenolic compounds are considered a serious environmental problem in soil and water contamination¹ because of their toxicity and widespread industrial use. Consequently, there is a great interest in the development of new methodologies for determination of phenols at trace levels in different areas of analytical chemistry.

Recently, solid-phase extraction (SPE) as a sample preparation technique has become very popular, being an alternative to the laborious and time-consuming liquid–liquid extraction.² Most of the applications have been performed with *n*-alkyl silicas,³ in these cases the efficiency of the

extraction process is highly dependent of the polarity of the analyte. It has been reported⁴ that recoveries are low when C18 silica is used to extract polar compounds.

The development of new sorbent materials plays a central role in the improvement of the extraction process. Among the compounds to incorporate in solid phase the metalloporphyrins appear as a very attractive option because they have rich coordination chemistry, allowing the inclusion of additional ligands. Meyerhoff et al. have reported various metalloporphyrins covalently linked to silica; they showed an increasing degree of histidine retention highly dependent of the specific metal ion in the center of the protoporphyrin.⁵

We have reported a chemically modified electrode (CME) prepared by electropolymerization of Ni-Protoporphyrin IX dimethyl ester {M(PPIX)}⁶ (Fig. 1), which showed an enhanced response for the oxidation of different phenolic compounds. This effect was attributed to a π – π interaction between the macrocycle and the benzene ring as

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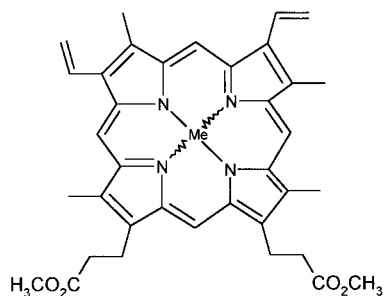


Figure 1 Structure of M-Protoporphyrin IX dimethyl ester.

much as an axial coordination binding related to the —COH group.⁷ The electroinitiated polymerization of the metalloporphyrin continued in solution leading to a black solid, highly insoluble polymer,⁸ which has similar IR spectra to the film deposited on the electrode, suggesting the same structural characteristics.

Under light of these results we have been attracted to the idea of using the highly insoluble polymeric material as a solid phase for the extraction of phenolic compounds from water.

The work reported herein is a preliminary study. Future research will include the immobilization of the Poly[Metalloprotoporphyrin IX] on particulate supports, to be incorporated to syringe barrel or SPE cartridges.

EXPERIMENTAL

Chemicals

Phenols were obtained from the following sources: 4-nitrophenol from Fluka (Buchs, Switzerland), 4-aminophenol from Mallinckrodt (St. Louis, MO), *p*-cresol from May & Baker Ltd. (Dagenham, England), 4-chlorophenol from Merck (Darmstadt, Germany), and BPA (4,4'-isopropylidene diphenol) from Aldrich (Milwaukee, WI). Standard solutions of phenols 100 mM were prepared in water; aliquots of the standard solutions were further diluted with doubly distilled water to appropriate concentrations.

Polymer Preparation

The different Poly[M-protoporphyrin IX] were prepared by electrosynthesis: 11 mL of 1.5 mM solution of metalloprotoporphyrin IX dimethyl ester (M-PP) in 0.1 M tetrabutylammonium perchlorate (TBAP)/CH₂Cl₂ was electrolyzed (1.1 V

vs. SCE) during 15 h and then was added to 5 mL of FePP (2 mM) in the same solvent. The mixture was left 24 h at room temperature, and a black solid was recovered.

Polymer Characterization

The IR and UV-Visible spectra of this material show a typical porphyrin ring pattern slightly broader than the monomer, which is consistent with a porphyrinic backbone.⁸ The vinyl C—C stretching vibration at 1625 cm⁻¹ (IR spectra) is diminished in the polymeric material, indicating that at least one of the vinyl groups is involved in the binding.

The specific surface area of the polymer was determined by Brunauer-Emmett-Teller (BET) measurement with nitrogen to be 238 m² g⁻¹. The average particle diameter was 30 μm.

Chromatographic Studies

The components of the liquid chromatography system used consisted of a 20-μL fixed loop injector (Rheodyne, Cotati, CA), a Perkin Elmer Series 10 high-pressure system, and a model LC-75 scanning spectrophotometric detector (Perkin-Elmer, Norwalk, CT). The chromatographic separation was carried out on a C18 bonded column (Hewlett Packard) 5 μm, 200 × g, 4.6 mm. A mobile phase consists of ethanol/water (50 : 50, v/v) was used at a flow rate of 0.5 mL · min⁻¹. A precolumn packed with C18 bonded silica gel (particle size 35–40 μm) was used.

All solvents were of HPLC grade purity and were filtered through a 0.22-μm filter (Millipore, Bedford, MA). Standard solutions in the 0.05–5 mM range for each phenol were prepared. Linear-regression analysis of peak heights from individual chromatograms vs. phenolic concentrations were performed for each standard solution, this data were used to calculate the concentration of each phenolic compound in the samples.

Batch Isotherms

The appropriate polymer (20 mg) was added to flasks containing various amount of phenol in water, in a final volume of 2 mL. The flasks were shaken at least 6 h to be sure that the system was equilibrated. Samples (1 mL) were removed and centrifuged (5000 × g for 2 min), and the supernatant was assayed for phenol concentration. The amount of phenol bound to the polymer (*q*^{*}) was calculated as the difference between the phenol concentration at the beginning of the experiment

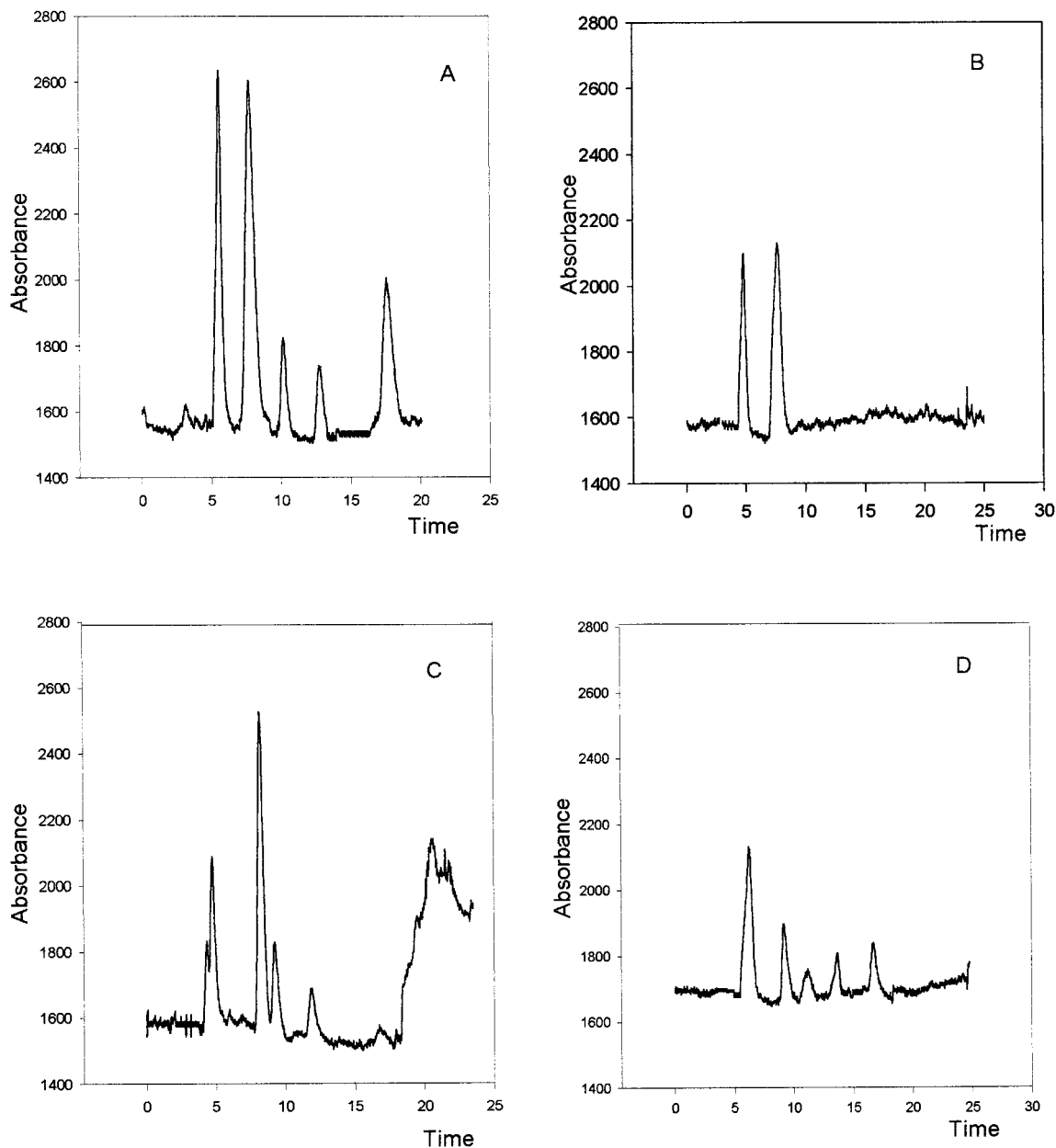


Figure 2 Chromatographic separation: (A) of a solution containing five phenolic compounds (*p*-aminophenol, *p*-nitrophenol, *p*-cresol, *p*-chlorophenol, and biphenyl). (B) After extracting previous solution with the polymer. (C) After liquid–liquid extraction, (D) after SPE with cartridges of C18-bonded silica coatings.

and the amount still present in the aqueous phase at equilibrium.

Data Acquisition and Manipulation

Sigma Plot for Windows v 4.0 was used for some of the data manipulation and for generation of the plots shown in all figures; making use of the experimental data and calculated values (q^* , C^*) eq. (1) was fitted for each compound. From the anal-

ysis of the Langmuir isotherms, the parameters K_{SPE} and qm were determined from straight-line plots of C^*/q^* against C^* . The intercept of such plots on the C^* axis is $-1/qm K_{\text{SPE}}$. The slope is $1/qm$.

Water Sample

Distilled water was spiked with standard phenolic solution. This sample was used during recovery experiments.

Table I The Recovery Efficiencies of Several Phenolic Compounds

Compounds	Cartridges LC-18 Octadecyl ^a	Liquid-Liquid Extraction ^a	Polymeric Metalloporphyrin ^a
<i>p</i> -Aminophenol	37 ± 5	50 ± 5	43 ± 5
<i>p</i> -Nitrophenol	76 ± 3	23 ± 5	53 ± 5
<i>p</i> -Cresol	70 ± 5	57 ± 2	98 ± 1
<i>p</i> -Chlorophenol	33 ± 5	33 ± 5	98 ± 1
Bisphenol A	66 ± 1	86 ± 1	98 ± 1

^a% recovery with 95% confidence interval with $n = 5$.

Extraction Procedures

Liquid-Liquid Extraction (EPA Method 604)

Before extraction, pH was adjusted to 1–2 with H₂SO₄. The sample (2 mL) was extracted three times with methylene chloride (2 mL) in a separator funnel. The fractions were combined and evaporated to dryness. The volume was made up to 2 mL with the mobile phase.

Cartridges LC-18 Octadecyl (100 mg, J. T. Baker)

Before use, cartridges were washed with 2 mL of acetonitrile to remove impurities. They were then conditioned with two 5-mL portions of methanol and left to soak for 1 min before methanol was drawn off; excess of methanol was subsequently displaced with 2 mL of deionized water at pH 2. The water sample (2 mL) was passed through the column. Elution was performed with 2 mL of methanol and assayed for phenolic concentration in the eluted solution.

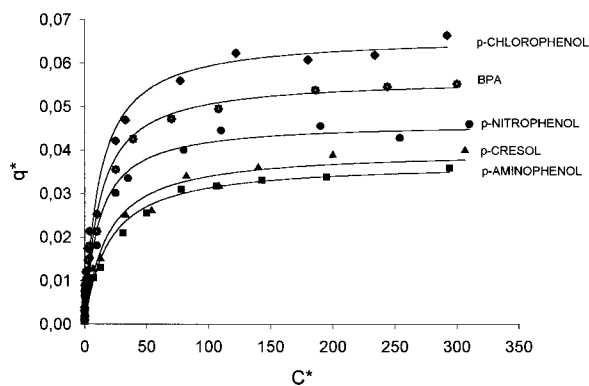


Figure 3 Sorption isotherms for the interaction of a variety of phenols and the polymer of Co-Protoporphyrin IX, 20 mg of polymer was added to 2 mL of each phenolic solution.

Polymer Extraction

Co-PPIX polymer (100 mg) was added to a tube containing 2 mL of sample solution. The tube was shaken 6 h. Sample (1 mL) was removed and centrifuged (5000 × *g*, for 2 min) and the supernatant assayed for phenol concentration. The phenols can be easily released from the polymer suspending the sorbent in pure methanol.

RESULTS AND DISCUSSION

The electro-oxidation of certain metal complexes of protoporphyrin IX in methylene chloride and tetrabutylammonium perchlorate (TBAP), maintaining the working electrode on a sufficiently positive potential to oxidize the porphyrin ring, leads to the deposition of electroactive porphyrin films on the electrode surface. Deposition continues after the current is interrupted, in a mechanism involving electroinitiated cationic vinyl polymerization.⁹ This reaction continues in the solution yielding a black solid material, very insoluble polymer, which has been characterized by IR and UV-Vis.⁸

Table II Values of Equilibrium Distribution Constants K_{SPE} and Maximum Capacity of the Sorbent (qm) for Phenolic Compounds Obtained from Straightline Plots of C^*/q^* Against C^*

Phenolic Compound	qm (mg/mg)	K_{SPE} (mg/L) ⁻¹
<i>p</i> -Chlorophenol	0.0664	8.4410 ⁻²
BPA	0.0566	8.3510 ⁻²
<i>p</i> -Nitrophenol	0.0465	8.9110 ⁻²
<i>p</i> -Aminophenol	0.0370	5.2810 ⁻²
Cresol	0.0400	5.6410 ⁻²

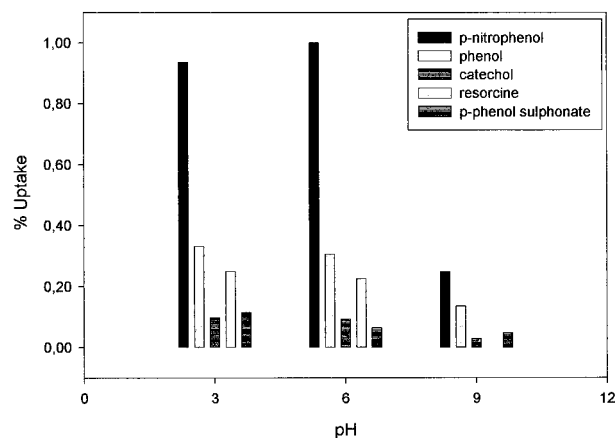


Figure 4 Dependence of the % uptake on the pH of the solution for five phenolic compounds, 20 mg of polymer was added to 2 mL of aqueous phenolic solution at three different pH values.

A reversible type 2 isotherm was obtained during Brunauer-Emmett-Teller (BET) measurement with nitrogen, indicating nonporous or macroporous material.¹⁰

Figure 2 is illustrative of the performance of the metalloporphyrin polymeric material in comparison with other standard methods for water analysis.¹¹ Figure 2(A) is a chromatographic separation of a solution containing five phenolic compounds (*p*-aminophenol, *p*-nitrophenol, *p*-cresol, *p*-chlorophenol, and BPA). Figure 2(B) shows the result of extracting previous solution with the polymer; this method is also compared with liquid-liquid extraction [Fig. 2(C)], which is an EPA approved technique described for nonvolatile compounds in water samples. Finally, Figure 1(D) shows the typical procedure of SPE using cartridges of C18-bonded silica coatings.

Clearly, the polymeric metalloporphyrin has removed most of the phenolic compounds present in the sample, and compares satisfactorily with the other extraction methods. This material can be reused many times, its adsorption capacity was not affected by several retention/elution cycles. Additionally, it does not release impurities in contact with organic solvents or water.

To quantify the extractive process, we prepared Table I, where the recovery efficiencies of several phenolic compounds are given.

As could be expected, *p*-aminophenol has the lowest recovery efficiency because its high polarity, even though the uptake of metalloporphyrin polymer is similar to the other phases. The selectivity of the extractive process was evaluated

comparing the correlation of % uptake between the two solid phases, C18 and polymeric porphyrin, the Pearson regression coefficient is very low ($r^2 = 0.07$), indicating a completely different behavior.

Sorption isotherms were measured for the interaction of a variety of phenols and the polymer of Co-Protoporphyrin IX (Fig. 3). The curves satisfactorily fit the Langmuir model,¹² and the analyte concentration in the solid phase at equilibrium (q^*) will vary with the concentration in the aqueous phase in a manner described by

$$q^* = q_m \cdot c^*/(1/K_{\text{SPE}} + c^*)h \quad (1)$$

where C^* is the concentration in the aqueous phase, q_m is the maximum capacity of the sorbent, and K_{SPE} is the equilibrium distribution constant between the solid and the aqueous phase.

The affinity of the polymeric metalloporphyrin for different phenolic compounds K_{SPE} and q_m are summarized in Table II, to estimate the selectivity of the method.

The values of K_{SPE} and q_m were obtained as described in the Experimental part.

The polymeric phase has similar K_{SPE} values for the hydrophobic compounds, and a significant lower value for the more hydrophilic *p*-aminophenol and cresol. Probably a more selective polar phase is required for the efficient uptake of the two last compounds.

The Figure 4 shows the dependence of the % uptake on the pH of the solution for five phenolic compounds, showing that the higher response is obtained when it is poorly dissociated, pH 3 to 6.

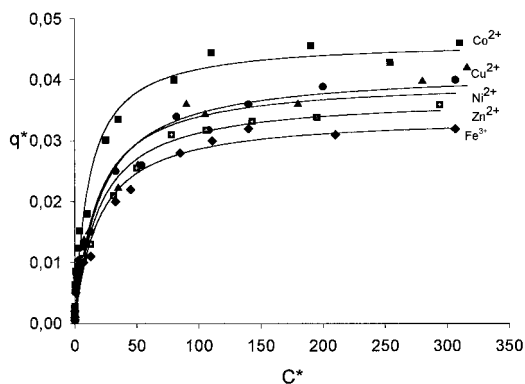


Figure 5 The sorption isotherms for the uptake of p-nitrophenol using different metalloporphyrin polymers as the solid phase, 20 mg of polymer was added to 2 mL of aqueous phenolic solution.

Table III K_{SPE} and qm Values, Obtained as Above for Different Metalloporphyrins

Poly[M-(PPIX)]	qm (mg/mg)	K_{SPE} (mg/L) ⁻¹
Co(II)	0.0465	8.9110 ⁻²
Cu(II)	0.0416	4.9310 ⁻²
Ni(II)	0.0400	5.6510 ⁻²
Zn(II)	0.0372	5.2910 ⁻²
Fe(III)	0.0341	5.2510 ⁻²

To evaluate the relevance of the specific metal ion in the center of the protoporphyrin, we prepared different polymeric poly[M-(PPIX)], being M = Co²⁺, Cu²⁺, Zn²⁺, and Fe³⁺. The sorption isotherms for the uptake of nitrophenol using these polymers as solid phases are shown in Figure 5 and the K_{SPE} and qm values, obtained as above, are reported in Table III.

A correlation of the stereochemistry of the coordinating groups in metalloporphyrins with the d electron configuration in the valence shell of the metal has been reported,¹³ showing that Fe³⁺ is the most reactive central metal to incorporate axial ligands. The d⁹ and d⁸ metalloporphyrins represented by Ni²⁺ and Cu²⁺, are four coordinated with planar or nearly planar configuration, allowing addition of axial ligands only to a limited extent. The d⁷ configuration, represented by Co²⁺ is intermediate in reactivity.

The slightly different K_{SPE} values observed in Table III suggest that even though an axial ligand-metalloporphyrin binding could contribute to the extraction process the strength of the interaction mainly depends on the π - π bonds, considering that the retention behavior is sensitive to changes in the solute electron density (Table II).

CONCLUSIONS

A metalloporphyrin polymeric material has been explored as solid phase extraction of phenolic

compounds. It was found to significantly improve the extraction efficiency of moderately polar phenolic compounds (40 to 60 mg/g polymer). The higher uptake is obtained for hydrophobic phenols, and when the molecules are poorly dissociated, pH 3 to 6.

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