

Use of Crosslinked Poly(ferric acrylate) as a Sorbent in Solid-Phase Extraction

K. SREENIVASAN

Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences & Technology, Poojapura, Trivandrum 695012, India

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ABSTRACT: A sample-preparation step, before chromatographic analysis, is frequently performed to enrich the components of interest from a complex matrix. This step is also needed to purify and concentrate the analyte present in a highly dilute medium. Solid-phase extraction (SPE) with a specific sorbent is one of the most widely used techniques for extracting trace components from aqueous or nonaqueous media. In this method, analytes are extracted by the passage of the medium through a cartridge containing a solid matrix. The recovery of the analytes from the medium considerably depends on the extent of the interactions between the analytes and the sorbent. Through the enhancement of these interactions, the extent of the uptake of the analytes can be improved. Poly(acrylic acid) is commonly employed as the sorbent in SPE for the isolation of polar analytes. This article discusses the use of the metal-containing polymer poly(ferric acrylate) as the sorbent for the isolation of a few phenols as representative components from water. The results indicate that the metal-containing polymer has an enhanced adsorption capacity in comparison with the capacity of the widely used sorbent poly(acrylic acid). © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2184–2187, 2002

Key words: poly(acrylic acid); poly(ferric acrylate); solid-phase extraction; phenols; EGDMA; ferric hydroxide; micro-bondapak

INTRODUCTION

In the routine analysis of samples with analytical techniques, a sample-preparation step is often necessary to isolate the components to be analyzed and to purify and concentrate the analytes.¹ Even today, sample-preparation methodologies are based on cumbersome solvent-extraction methods. Problems associated with these traditional sample-preparation methods, such as the use of toxic organic solvents and multistep procedures, which often result in the loss of analytes during these processes, fre-

quently make sample preparation the major source of error in the analysis.

The idea of using sorbent materials to extract trace organics from aqueous matrices was developed long ago.² One of the most important features of this technique is the concentration of the analyte by the sorbent. With a sorbent that has a strong affinity for organic compounds, such compounds can be enriched from an otherwise very dilute phase. The method known as *solid-phase extraction* (SPE) is one of the most commonly used sorbent-extraction techniques. SPE with small cartridges containing sorbents is now established as an important sample-preparation technique for either matrix simplification or trace enrichment.

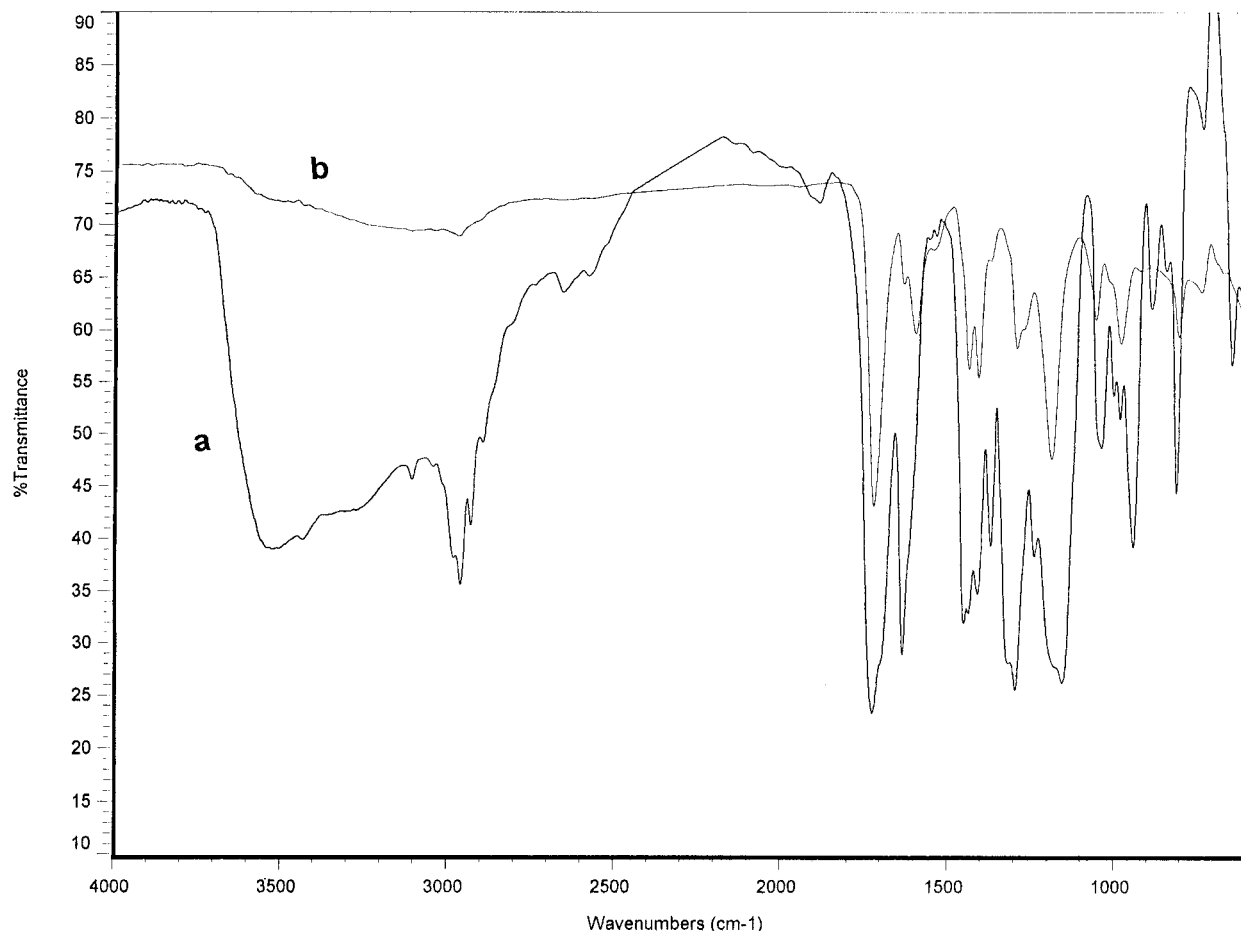


Figure 1 Infrared spectra of (a) poly(acrylic acid) and (b) poly(ferric acrylate).

SPE does have some limitations, however, such as low recovery. The sorbents available today are largely based on poly(acrylic acid) for polar compounds and poly(dimethyl siloxane) for nonpolar compounds. The recovery of the analyte from the sample matrix, to a large extent, is governed by the interaction of the sorbent and the analyte. One straightforward approach to enhancing the recovery is to increase the interaction between the sorbent and the analyte, which can be achieved with a modified sorbent. This article discusses the use of a chemically modified acrylic acid, ferric acrylate, as a sorbent in SPE. The recovery of a few phenols from water with the new sorbent is compared with the widely used sorbent poly(acrylic acid).

EXPERIMENTAL

Chemicals

Acrylic acid and ethylene glycol dimethacrylate (EGDMA) were procured from Fluka (Germany).

The stabilizers were removed from the monomers before use. Other analytical-grade or chromatographic-grade chemicals were from SD Fine Chemicals (Bombay, India). *ortho*-Nitrophenol, *ortho*-chlorophenol, and phenol were from Emerck (Bombay, India).

Preparation of the Polymers

Ferric hydroxide was prepared by the treatment of ferric chloride with sodium hydroxide. The precipitated ferric hydroxide was collected and washed extensively with water to remove the unreacted alkali. The compound was then washed with acetone and dried. A stoichiometric quantity of acrylic acid and ferric hydroxide were reacted in dichloromethane. After the completion of the reaction, EGDMA was added as a crosslinker (the added amount was 30% of the amount of ferric acrylate). The polymerization was initiated by γ irradiation from a panoramic batch irradiator (BARC, Bombay, India). The total dose was 0.5 Mrad at a rate of 0.2 Mrad/h. Poly(acrylic acid)

was prepared similarly. After the polymerization, the polymers were crushed into powders. Particles (100–200 μm) were collected and placed in acetone for 48 h. The polymers were then dried at 50°C in a vacuum oven.

Instrumental

A high performance liquid chromatography system (Waters Associates, Inc.) consisting of a model 510 solvent delivery pump, a model 7725 Reodyne injector, and a model 486 variable-wavelength detector was used for the chromatographic analysis. A u-bondapak C_{18} column in conjunction with a mixture of methanol and water (75:25 v/v) as the mobile phase at a flow rate of 1 mL/min was used for the chromatographic separation of the phenols. The eluted compounds were detected at 245 nm.

Interaction of the Polymers with the Phenols

The polymers (100 mg) were placed in 100-mL aqueous solutions of the phenols (the concentration of the phenols was 100 $\mu\text{g}/\text{mL}$) at room temperature (30°C) with occasional shaking. After 30 min, the polymers were collected from the solu-

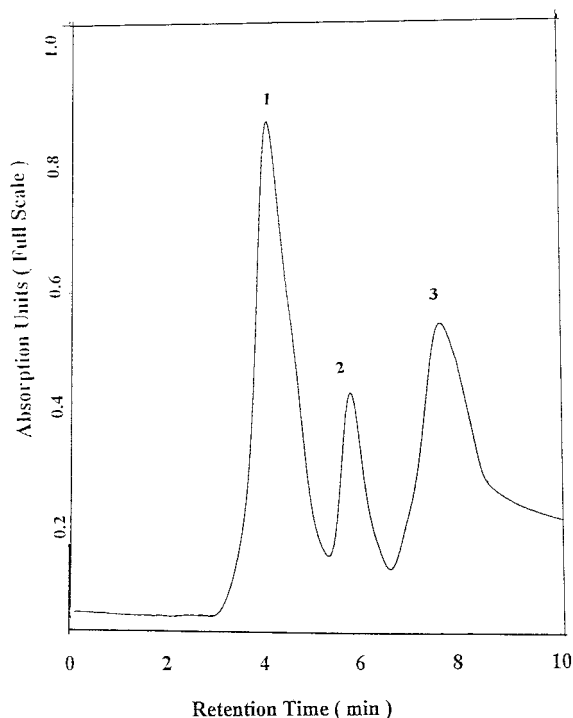


Figure 2 Typical chromatogram of a mixture of *ortho*-nitrophenol (peak 1), *ortho*-chlorophenol (peak 2), and phenol (peak 3).

Table I Extent of Uptake of Phenols by the Sorbents ($\mu\text{g}/100 \text{ mg}$)

Sorbent	Phenol	Chlorophenol	Nitrophenol
Poly(acrylic acid)	930 \pm 12	1221 \pm 9	1926 \pm 8
Poly(ferric acrylate)	1559 \pm 21	2342 \pm 16	3936 \pm 7
Increase (%)	68	92	104

tions by filtration and then placed in 20 mL of acetone for 30 min at an elevated temperature (45°C). The acetone was decanted into a beaker, and 20 mL of fresh acetone was added to the polymer. The process was repeated three times. The combined acetone (from three extractions) was evaporated to dryness. The residue was dissolved in 10 mL of a methanol–water mixture (the same as the mobile phase). The solution (50 μL) was injected into the column.

RESULTS AND DISCUSSION

Figure 1(a) shows the infrared spectrum of the acrylic acid. The broad band centered around 3400 cm^{-1} and associated with the $-\text{COOH}$ group of acrylic acid is absent in ferric acrylate [see Fig. 1(b)], indicating a reaction between ferric ions and $-\text{COOH}$ groups. The presence of iron in the polymer is further confirmed by energy-dispersive X-ray analysis (data not shown here).

Figure 2 depicts the chromatogram of the three phenols: nitrophenol, chlorophenol, and phenol. Table I summarizes the quantities of the phenols adsorbed by the polymers. There is a substantial increase in the uptake of phenols from water by the sorbent based on ferric acrylate in comparison with the uptake by the poly(acrylic acid) sorbent. The percentage increase in the adsorption of phenols by the poly(ferric acrylate) matrix in comparison with the poly(acrylic acid) sorbent is also shown in Table I.

Several factors can influence the quantity of analytes extracted by the sorbent in SPE. The prominent factor may be the characteristics of the sorbent. Because both the sample matrix and the sorbent are competing for the analytes, the affinity of the sorbent for the analytes is crucial for improved adsorption. For polar analytes such as phenols, the sorbent should be polar in nature. The sorbent based on the metal-containing mono-

mer discussed here adsorbs significantly higher quantities of phenols from water, presumably through enhanced interactions.

An interesting trend observed in the study is the influence of the polarity of the analytes on the extent of adsorption. The extent of adsorption increases in the order nitrophenol > chlorophenol > phenol. The polarity of these compounds also increases in the same order. The speed of interaction, together with the extent of adsorption, is an important factor in determining the efficiency in SPE. The data indicate that the simple modification of the monomer before polymerization remarkably improves the extent of the interaction between the sorbent and the target analytes.

Metal-containing polymers have been used for diverse applications.³ Polymers based on heavy metals and primarily tin have been used in the production of antifouling coatings. Metal-containing polymers have been employed as electrolytes and also in the development of metal-ion-recognizing entities.^{4,5} This study shows that polymers based on the metal-containing monomer could be used in the generation of matrices with improved adsorption capacities. Such materials may ultimately be employed as sorbents in SPE.

In the clinical, environmental, and industrial fields, the analysis of entities in complex matrices frequently requires pretreatment steps. SPE is the most convenient and simple methodology to

concentrate or isolate a target molecule from a dilute or complex matrix. The sorbents prepared here are highly crosslinked, virtually nonswelling, and compatible with aqueous, nonaqueous, alkaline, and acidic phases, indicating the wide applicability of the sorbent material. It seems that the use of the metal-containing monomer as a sorbent in SPE improves the sorbent-water partition coefficients, thereby enhancing the adsorption rate of the analytes. By varying the quantity of the crosslinking agent, we can prepare polymers with varied properties. We believe that such polymers, even though we have not studied them, could be used as coatings in widely practiced solid-phase microextraction techniques.

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