



Electroplating of nanostructured polyaniline–polypyrrole composite coating in a stainless-steel tube for on-line in-tube solid phase microextraction



Hamid Asiabi^a, Yadollah Yamini^{a,*}, Shahram Seidi^b, Ali Esrafilic^c, Fatemeh Rezaei^a

^a Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

^b Department of Analytical Chemistry, Faculty of Chemistry, K.N. Toosi University of Technology, Tehran, Iran

^c Environmental Health Engineering Department, School of Public Health, Iran University of Medical Sciences, Iran

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ABSTRACT

In this work, a novel and efficient on-line in-tube solid phase microextraction method followed by high performance liquid chromatography was developed for preconcentration and determination of trace amounts of parabens. A nanostructured polyaniline–polypyrrole composite was electrochemically deposited on the inner surface of a stainless steel tube and used as the extraction phase. Several important factors that influence the extraction efficiency, including type of solid-phase coating, extraction and desorption times, flow rates of the sample solution and eluent, pH, and ionic strength of the sample solution were investigated and optimized. Under the optimal conditions, the limits of detection were in the range of 0.02–0.04 $\mu\text{g L}^{-1}$. This method showed good linearity for parabens in the range of 0.07–50 $\mu\text{g L}^{-1}$, with coefficients of determination better than 0.998. The intra- and inter-assay precisions (RSD%, $n = 3$) were in the range of 5.9–7.0% and 4.4–5.7% at three concentration levels of 2, 10, and 20 $\mu\text{g L}^{-1}$, respectively. The extraction recovery values for the spiked samples were in the acceptable range of 80.3–90.2%. The validated method was successfully applied for analysis of methyl-, ethyl-, and propyl parabens in some water, milk, and juice samples.

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1. Introduction

The ever-growing use of technology in our daily life causes production of environmental pollutants, which can be potentially life-threatening for living organisms. Thus, fast and precise determination of trace amounts of different analytes has received significant attention in recent years. Accordingly, development of new sample preparation techniques with higher sensitivity and better accuracy of analysis is the subject of many studies in various fields.

Alkyl and aryl esters of *p*-hydroxybenzoic acid are commercially known as parabens [1]. Parabens comprise a group of compounds widely used as antimicrobial preservatives in food, pharmaceutical, and cosmetics products; mainly because of the broad antimicrobial spectrum, good stability, non-volatility, and effectiveness in a wide pH range [2]. The extensive usage has raised concerns about their potential long-term effects on human health and wildlife; especially as they are weak endocrine disruptors [3]. Thus, simple and

sensitive analytical methods are required to understand the fate and distribution of this group of contaminants in the environment.

Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are the most frequently employed sample preparation techniques. Modern trends in analytical chemistry are moving toward simplified and miniaturized sample preparation methods providing simultaneous sample clean-up and analyte preconcentration. Among these methods, solid phase microextraction (SPME) is a fast alternative technique for conventional extraction systems, which can be used for both portable sampling (field analysis) and sample preparation aims.

In SPME, an absorptive coating is used as the extraction medium and the analytes are preferentially absorbed on its surface. Since its introduction in early 1990s by Arthur and Pawliszyn [4], a lot of developments have been introduced for the technique that can generally be classified into two areas; sorbent development or coating technology and automation.

In general, most commercial SPME coatings suffer from fragility, low thermal and chemical stability, and low selectivity for the target analytes. These points are some important criteria to be considered in preparation of new SPME coatings. The discovery of conducting polymers has opened up many new possibilities in

* Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.
E-mail address: yyamini@modares.ac.ir (Y. Yamini).

SPME. These polymers can be synthesized either chemically or electrochemically. The first attempt in electrochemical synthesis of conducting polymers as SPME coatings was reported by Wu and Pawliszyn [5]. Electrochemically coated tubes exhibit several advantages including higher extraction efficiency, better thermal and mechanical stability, and easy controllable film thickness and morphology by alteration of different parameters such as electrolyte concentration, applied potential, and polymerization time [6–11]. Also, this method is especially attractive due to the possibility of deposition onto complex shape substrates like inner surface of a capillary tube, high purity of the deposits, low-temperature processing, and low-cost equipment [12,13].

Among the conducting polymers, polyaniline (PAN) and polypyrrole (PPY) are probably the most widely studied ones considering their adjustable properties [12,14–16]. These polymers exhibit multifunctional and permeable porous structures, which provide different intermolecular interactions such as acid–base, π – π , dipole–dipole, hydrophobic, and hydrogen bonding, as well as exchange among the polymers and the analytes [12,15,16].

Successful on-line combination of SPME to HPLC was reported using in-tube SPME by applying an inner surface of a coated capillary [17]. After this report, many commercial (such as a piece of GC capillary columns) and synthesized coated tubes were employed for in-tube SPME–HPLC [18–23]. In-tube SPME provides convenient automation of the extraction process, reduced analysis time, and improved precision and sensitivity in comparison with manual off-line techniques.

In the present study, instead of applying conventional time-consuming methods such as sol–gel for synthesis of in-tube SPME coating, a new method was developed to use conductive polymers in in-tube SPME. Nanostructured polypyrrole (PPY), polyaniline (PAN), and polypyrrole–polyaniline (PPA) composite coatings were electrochemically deposited on the inner surface of a stainless-steel tube as the unbreakable substrate. In comparison with chemical methods, reducing the time required for synthesis of coating to 20 min is a considerable advantage for electrochemical approaches. Another advantage is that it is possible to use conductive polymers and electrochemistry methods in in-tube SPME methods. To the best of our knowledge, there is no report about electrochemical synthesis of an in-tube SPME coating film in the literature. Also, the use of a nanostructured polypyrrole–polyaniline composite coating has not been reported as the extracting phase in SPME.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical reagent grade. Standards of methylparaben (MP), ethylparaben (EP), and propylparaben (PP) were obtained from Sigma–Aldrich (St. Louis, MO, USA). N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was purchased from Sigma–Aldrich. The stock solutions of the parabens (1000 mg L^{-1}) were prepared by dissolving 10 mg of the compounds in 10 mL methanol. A mixed standard solution of parabens was prepared by adding an appropriate amount of each stock standard solution to a 25-mL volumetric flask and diluting to the mark by methanol. All standard solutions were stored at 4°C and protected from the light. HPLC-grade methanol and acetonitrile were purchased from Caledon (Georgetown, ON, Canada). Synthetic pyrrole and aniline were obtained from Aldrich (Milwaukee, WI, USA). Ultra-pure water was produced on a Youngling ultrapure water purification system model Aqua MaxTM-ultra (Seoul, South Korea). Other chemicals applied were of the analytical reagent grade or of the highest purity available. Plastic and glassware used for the experiments were previously washed with acetone and rinsed carefully with ultra-pure water.

2.2. Apparatus

Particle size and morphology of the synthesized NPs were determined by a scanning electron microscope (SEM) model EM3200 from KYKY Zhongguancun (Beijing, China). Chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Cheminert HPLC valve from Valco (Houston, TX, USA) with a $20\text{-}\mu\text{L}$ sample loop and equipped with a Varian 9050 UV–Vis detector. Chromatographic data were recorded and analyzed using Chromana software (version 3.6.4). The separations were run on an ODS-3 column ($250 \text{ mm} \times 4.6 \text{ mm}$, with a $5\text{-}\mu\text{m}$ particle size) from Hector Company (Daejeon, Korea). A mixture of ultra-pure water and acetonitrile (50:50) at a flow rate of 1.0 mL min^{-1} was applied as the mobile phase and the analytes were detected at 254 nm. All the pH measurements were performed with a WTW Inolab pH meter (Weilheim, Germany). GPFA1-380 peristaltic pump from Ultra-Voltammetry Company (Tehran, Iran) was applied to pass the solutions through the stainless steel capillary tube.

2.3. Preparation of polymer-coated capillary tubes

In the present work, two different types of monomers were used for synthesis of capillary tubes. Three types of polymer films including polypyrrole, polyaniline, and polypyrrole/polyaniline (composite) were deposited on the inner surface of the stainless steel tube using a three-electrode system. A stainless steel tube (10 cm length and 0.75 mm diameter) was used as the working electrode; Pt and saturated Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. A peristaltic pump was used to deliver the monomer solution from the inner surface of the stainless steel tube. Before electrochemical deposition, the steel tubes were cleaned by acetone and HPLC-grade water and finally air dried at the room temperature. The PPY, PAN, and PPA films were deposited on the inner surface of the stainless steel tube by applying a potential of +1.2 V for 10 min in an aqueous solution containing 0.2 M pyrrole, 0.2 M aniline, and 0.2 M pyrrole/aniline (1:1, v/v) monomers, respectively. The concentration of oxalic acid was kept constant at 0.3 M (oxalate ions were used as anion dopants in the conducting polymers). Actually, charge neutrality is maintained by the dopant anions in the polymer chain [24,25]. After electrochemical deposition, the steel tube coated with PPY, PAN, and PPA films were washed with methanol, acetone, and water in sequence and dried under nitrogen gas flow. Growth of the films was controlled based on the amount of charge consumed in the electropolymerization [24–27].

2.4. On-line in-tube SPME–HPLC procedure

A schema of complete assembly of the extraction unit and operation mode is shown in Fig. 1. The coated stainless steel tube was mounted on valve 1 (V_1) in the position the loop was originally positioned. Both V_1 and V_2 valves were initially set at the load position (red arrows). Pump A was on to flow the sample solution through the tube at 11.0 mL min^{-1} and pump B was off. The effluent of V_1 was again poured into the sample compartment after passing through the coated tube. In other words, the procedure was carried out in a circulating path. Also, the HPLC mobile phase was directly passed through the analytical column at 1.0 mL min^{-1} by pump C to obtain a stable baseline for chromatographic separation. After extraction for a given time interval, V_1 was directed to the injection position, pump A was turned off and pump B was turned on to flow the desorption solvent through the tube at 7.0 mL min^{-1} . The effluent of desorption solvent was circulated the same as the extraction procedure to reach the maximum desorption efficiency (blue arrows). Finally, after a given desorption time interval, pump B was

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