Analytica Chimica Acta 798 (2013) 48–55

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

A new strategy for synthesis of an in-tube molecularly imprinted polymer-solid phase microextraction device: Selective off-line extraction of 4-nitrophenol as an example of priority pollutants from environmental water samples

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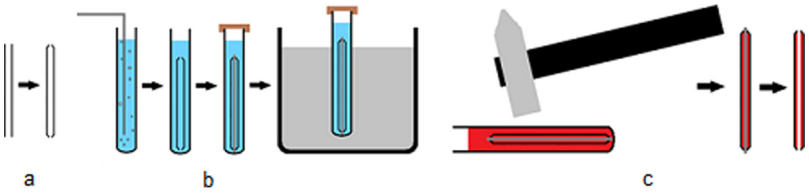
HIGHLIGHTS

- A new simple method has been developed for the construction of an in-tube molecularly imprinted polymer-solid phase microextraction device.
- Aim to optimize this new proposed method, different parameters were assessed and optimized.
- At optimized conditions, the matrix effects and cross selectivity of the new MIP micro tubes were evaluated.
- New MIP-SPME and standard SPE methods were applied for real water sample.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form 21 August 2013
Accepted 23 August 2013
Available online 4 September 2013

Keywords:
In-tube
Solid phase microextraction
Molecularly imprinted polymer
4-nitrophenol

ABSTRACT

In this study a novel preparation protocol has been developed for the construction of an in-tube molecularly imprinted polymer-solid phase microextraction (MIP-SPME) device. Open tubular capillaries have been molded from a polymer sorbent imprinted for 4-nitrophenol as target molecule. Different parameters like inner diameter and volume of the polymer, porogen volume, swelling and shrinking effects of the polymer tubes, polymerization time, pH of the sample, extraction time, 'salting out' effect and serial connection of the tubes were evaluated and optimized. Particularly, an optimized polymer preparation process and extraction condition enhanced the final extraction recovery of 4-nitrophenol substantially. Using this new MIP-SPME technique with high-performance liquid chromatography-ultraviolet (HPLC-UV) analysis of the extracts, the linear range and the limits of detection and quantification are 0.001–10 mg L^{-1}, 0.33 μg L^{-1} and 1.1 μg L^{-1} respectively. At optimized conditions, a mixture of nitrophenols, alkylated and chlorinated phenols spiked into municipal waste water were analyzed to evaluate the matrix effects and cross selectivity of the new MIP capillary tubes.

1. Introduction

Since the introduction of artificial antibody hypothesis in 1942 and the first use of a molecularly imprinted polymer (MIP) in 1972, these materials have been extensively studied [1–3]. MIP operates as an artificial specific receptor, owing to it's imprinting according

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0003-2670/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.aca.2013.08.038

to the size, shape and functional groups of a template molecule. In addition to the high selectivity of MIPs, their simplicity of production and furthermore, less strict operation conditions compared to immunosorbents, make their applications remarkably widespread.

Solid-phase microextraction (SPME) is a simple, fast, portable sampling and sample preparation method that uses smaller volumes of solvent and is solvent-free in some cases. Since its introduction in early 1990s [4], SPME has been developed in different types, including coated fibers and in-tube devices. Due to the fairly unspecific absorption or adsorption mechanisms in current SPME techniques, the enrichment of a broad variety of substances is the preferable application field of SPME. In general, commercial SPME polymer coatings possess a low selectivity toward a special target compound.

A combination of the selectivity of MIP materials with the simplicity of SPME can enable a tailor-made extraction performance of target molecules of special concern. Various methods were developed for preparing MIP-coated SPME fibers, which were used for analysis of brombuterol [5], triazines [6,7], Sudan dyes [8,9], ascorbic acid [10], tetracyclines [11], bisphenol A (BPA) [12], chloroacetanilide herbicides [13], anabolic steroids [14] and estrogens [15]. MIP-monolithic SPME fibers were evaluated via selective determination of triazines [16–18], methamphetamine [19], diacetylmorphine [20], ephedrine [21] and parabens [22]. In all these applications, the limited mechanic stability of the MIP fibers may cause short lifetimes and problems for multiple uses.

One approach for overcoming this problem would be in-tube SPME technique. Besides, handling in-tube techniques may be easier for automated on-line methods. First report for in-tube MIP-SPME was released by Pawliszyn and coworkers [23] for selective determination of propranolol. The MIP selected particles were used to pack a polyether ether ketone (PEEK) tube. Since then, different methods like monolith in-tube MIP-SPME [24–27], MIP modified-polypropylene hollow fiber [28], multiple fibers packed in-PEEK tube [29] were developed.

Due to its high toxicity impact on environment and human health, 4-nitrophenol is regulated as one of the priority pollutants by the US Environmental Protection Agency (EPA) [30]. 4-Nitrophenol has been used widely as an intermediate or precursor for the production of insecticides, pharmaceuticals and dyes. Thus the determination of 4-nitrophenol in complex samples has attracted much attention. Commercially available SPME fibers [31–36] and new generated SPME fibers [37–39] were used for its determination in water samples. Molecularly imprinted polymers were synthesized for 4-nitrophenol and evaluated for its determination in honey [40] and water [41–45] samples.

The objective of this study was to develop simple, inexpensive and reusable open-tubular MIP-capillaries for application in in-tube MIP-SPME. The novelty in contrast to the above mentioned packed or surface modified MIP-SPME is a new approach in synthesizing the MIPs as monolithic tube directly inside a glass capillary. This *in-situ* synthesis allows a wide variability of the MIP composition. The synthesized MIP-capillaries were evaluated for in-tube MIP-SPME extraction with HPLC-UV analysis of 4-nitrophenol from real water samples.

2. Materials and methods

2.1. Materials

The chemicals used for polymer synthesis and extraction experiments were 4-nitrophenol, acetic acid, hydrochloric acid (HCl), methanol and acetonitrile (ACN) from MERCK (Darmstadt, Germany). Ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), 2,2′-azobisisobutyronitrile (AIBN) and EPA 604 phenols mixture containing 4-chloro-3-methylphenol (4-C-3MP), 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4-dimethylphenol (2,4-DMP), 2,4-dinitrophenol (2,4-DNP), 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), pentachlorophenol (PCP), phenol (Ph), and 2,4,6-trichlorophenol (2,4,6-TCP) in methanol were obtained from Sigma-Aldrich (Steinheim, Germany). The monomer and AIBN were purified prior to use for synthesis. The other chemicals were used as delivered due to high enough purity.

The stock standard solution of 4-NP was prepared in water, pH 3, at a concentration of 500 mg L^{-1} and stored in the refrigerator. Other standard solutions were daily prepared via dilution of stock solution using pH adjusted deionized water.

2.2. Instrumentation

The analysis was performed using an HPLC instrument HP series 1100 of Hewlett Packard (Waldbronn, Germany) equipped with a binary pump, a membrane degasser, an autosampler and a diode-array UV detector (DAD). For separation, an Aqua C_{18} column (Phenomenex, Aschaffenburg, Germany) of 30 mm length and 2.00 mm I.D. (5 μm particle size) was applied. The eluent consisted of 85% water (pH 2.5, acetic acid) and 15% ACN (1% acetic acid) at 1 mL min^{-1}. The column temperature was adjusted at 22 °C. 5 μL of extracts were injected automatically. The DAD diode array detector operated at 320 nm (bandwidth: 40 nm) with a reference at 450 nm (bandwidth: 80 nm). Regularly blank and 4-NP standard analyses were carried out to check carryover effects and instrument performance.

KDS100 syringe pump from KD Scientific (Holliston, USA) was used to generate defined flows through the synthesized MIP-capillaries. A GFL water bath (Burgwedel, Germany) was used for the synthesis of the polymer tubes. 10, 20 and 100 μL glass-capillary tubes were prepared from BRAND (Wertheim, Germany). 2 mL glass vials and 250 μL micro glass vials (inserts) were used for collecting the samples.

2.3. Open-tubular MIP-capillary preparation

The method that is used for the preparation of MIP tubes is schematically shown in Fig. 1. Both tips of 10 and 20 μL glass-capillaries were coned with flame to the diameter sizes of 100 and 480 μm and were checked carefully with hand lens (Fig. 1a). Then one-side closed 100 μL capillary was filled with precursor polymer mixture that was described previously [41,43] and deaerated with helium for 10 min. The coned glass-capillary was placed inside the deaerated polymer mixture and the related metal rod was inserted in the middle of it. This technique allows a bubble-less load of the glass-capillary with the polymer mixture. The open side of 100 μL capillary was closed immediately and placed in a water bath that was adjusted at 60 °C (Fig. 1b). In summary for MIP preparation, 0.041 g of 4-NP, 0.01 g of AIBN, 1.17 g of EGDMA and 100 μL of MAA acid were dissolved in ACN as porogen. Non-imprinted polymer (NIP) mixture was prepared in the same way without the target molecule. For porogen volume evaluation, it was changed from 1.5 to 6 mL to increase the porosity of synthesized MIP-capillaries. After polymerization, the outer glass capillary was broken carefully; the excess polymer was removed from outside the glass-capillary later used as open tubular MIP/NIP device. The metal rod defining the internal diameter of the MIP tube was removed, whereupon a uniform polymer tube remained inside the glass capillary (Fig. 1c). 50 mL of methanol was passed through the tube with a flow of 5 mL h^{-1} to remove the template molecules and other unreacted precursors. The prepared tubes were stored in ACN when they were not used for extraction experiments..