



Highly porous nanostructured copper foam fiber impregnated with an organic solvent for headspace liquid-phase microextraction



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ABSTRACT

A new headspace liquid-phase microextraction technique based on using a copper foam nanostructure substrate followed by gas chromatography-flame ionization detection was developed for the determination of volatile organic compounds in water and wastewater samples. The copper foam with highly porous nanostructured walls was fabricated on the surface of a copper wire by a rapid and facile electrochemical process and used as the extractant solvent holder. Propyl benzoate was immobilized in the pores of the copper foam coating and used for the microextraction of benzene, toluene, ethylbenzene and xylenes. The experimental parameters such as the type of organic solvent, desorption temperature, desorption time, salt concentration, sample temperature, equilibrium time and extraction time, were investigated and optimized. Under the optimum conditions, the method detection limit was between 0.06 and 0.25 $\mu\text{g L}^{-1}$. The relative standard deviation of the method for the analytes at 4–8 $\mu\text{g L}^{-1}$ concentration level ranged from 7.9 to 11%. The fiber-to-fiber reproducibility for three fibers prepared under the same condition was 9.3–12%. The enrichment factor was in the range of 615–744. Different water samples were analyzed for the evaluation of the method in real sample analysis. Relative recoveries for spiked tap, river and wastewater samples were in the range of 85–94%. Finally, the extraction efficiency of the method was compared with those of headspace single drop microextraction and headspace SPME with the commercial fibers.

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1. Introduction

Among different sample pretreatment methods developed in recent years, liquid-phase microextraction (LPME), solvent-bar microextraction, stir-bar sorptive extraction (SBSE) and solid-phase microextraction (SPME) are attractive microextraction techniques used for the analysis of different compounds.

SPME is a solvent-free microextraction technique applicable for the extraction of analytes from various matrices including solid, liquid and gaseous samples. SPME was first introduced by Belardi and Pawliszyn in 1989 [1]. It is based on the partition of analytes between a sample matrix and a stationary phase coated on a fiber. The method is simple, sensitive, solvent free, portable, easy to automate and environmentally friendly [2,3]. SPME operates in three major modes: direct-immersion [4], membrane-protected SPME [5] and headspace (HS) [6–8]. Among these modes, HS-SPME is useful for the extraction of volatile and semi volatile organic compounds. This mode is also suitable for the extraction of ana-

lytes from samples with complex matrices [9]. In spite of the great applicability of SPME method, it has some major difficulties such as low chemical and mechanical coating stability, memory effect, expensive fibers, limited selection of commercially available fibers [10,11], fragility and limited lifetime of the fiber [12], and easy swelling in organic solvents [13]. Therefore, most attempts have been focused on obviating the disadvantages of SPME fibers by improving the selectivity, extraction ability and stability of SPME fiber by synthesizing new coatings [14,15]. Nevertheless, the synthesis procedures are relatively complex, time consuming and difficult [11]. SBSE is an environmentally friendly, simple and solvent-free sample preparation method which was first introduced by Baltussen et al. in 1999 [16]. The method, allows the extraction and preconcentration of the target analytes in a single step. SBSE is a sensitive, non-destructive, reliable, robust and generally speedy technique. The main limitation of SBSE is related to the unavailability of the commercial coatings. The laboratory made coatings are very effective for the extraction of polar analytes. However, their synthesis procedure is time-consuming and needs more laborious steps during the preparation procedure [17,18].

Solvent microextraction technique by which analytes are extracted into a single drop of organic solvent was introduced by

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Cantwell and Jeannot [19]. Subsequently, liquid phase microextraction in a few microliters of an organic solvent, using a conventional microsyringe was introduced by He and Lee in 1997 [20]. This LPME approach, which is known as single-drop microextraction (SDME), has been developed in different application fields [21]. In SDME, a micro drop of an organic solvent is suspended at the end of a microsyringe needle to extract the target analytes. There are two types of SDME: direct-immersion and headspace technique. SDME is quick, simple and inexpensive; it also avoids some problems of the SPME method such as sample carry-over [22]. It also needs simple equipment and in comparison with the limited number of SPME fiber coatings, there is a wide variety of organic solvents for SDME. SDME has been successfully used for the extraction and determination of many compounds such as chlorobenzenes, nitroaromatic explosives, alcohols, pesticides and volatile organic compounds (VOCs) in different samples [23,24]. In spite of the advantages of SDME, there are some limitations in SDME such as the instability of the solvent droplet, the dissolution of solvent during extraction in direct immersion mode and solvent evaporation in HS-SDME. In order to improve the stability of organic solvents during the extraction process, many attempts have been made to protect the organic extractant solvent. Microextraction techniques, including hollow fiber-protected LPME [25] and solvent bar microextraction [26], are two major microextraction methods used for the protection of organic solvents from sample matrices. In these techniques, the organic solvent is protected within a short length of a polymeric hollow fiber.

To overcome some SDME and SPME problems, a method based on the combination of solid- and liquid phase microextraction has recently been developed [27]. In this method, a thin film of an organic solvent was coated on the flower-like silica nanostructure created on the surface of a stainless steel wire. This wire was used as the SPME fiber. Some limitations of SPME, such as carry-over and stripping of the coating after several uses can be avoided by using this technique. Despite the clear advantages of this technique, the fabrication of the flower-like silica nanostructures procedure is relatively time consuming and involves more laborious steps during the preparation. Recently, an attempt has been made to form a microporous structure and use it as the extractant solvent holder. Zhang et al. introduced a novel, simple and fast one-step LPME approach, termed plunger-in-needle LPME [28]. In this method, the stainless steel plunger wire of a commercially available plunger-in-needle microsyringe was simply etched by immersion in hydrofluoric acid to form a microporous structure, and it served as the holder for extractant solvent. Although the etched stainless steel plunger wire has advantages such as larger surface area and better resistance to high temperature and pH, the etching procedure is still time-consuming.

Ramification of electrodeposited metals such as copper and tin has been a very interesting topic for scientists [29,30]. In particular, three-dimensional (3D) nanoramified metal deposits are suitable for sensors, supercapacitors, batteries and fuel cells [31]. In the present study, a simple and very rapid procedure was used to electrodeposit a copper foam coating with highly porous nanostructured walls on the surface of a copper wire [32]. The porous structure of coating was impregnated with propyl benzoate and used as an extracting phase holder for the extraction of BTEX (benzene, toluene, ethylbenzene and xylenes) as the model compounds from the headspace of water samples. To the best of our knowledge, this is the first time using highly porous copper foam for the microextraction purpose. The analytes were thermally desorbed from the fiber into the injection port of GC-flame ionization detection. The extraction and desorption were performed using a homemade SPME holder. Various experimental parameters affecting the extraction efficiency, such as the type of organic solvent, desorption temperature, desorption time, salt

concentration, temperature effect, equilibrium time and extraction time, were investigated and optimized. The method was compared with HS-SDME and HS-SPME (with the commercial PDMS fiber) in terms of performance. Finally, the method was applied for the analysis of BTEX in environmental water and wastewater samples.

2. Experimental

2.1. Chemicals and standard solutions

Methanol, acetone, benzene, toluene, ethylbenzene and *o*-xylene were purchased from Merck (Darmstadt, Germany). *m*-Xylene and *p*-xylene were prepared from Sigma & Aldrich (St. Louis, USA). Other reagents were also obtained from Merck and all of them were of analytical grade. Stock standard solutions were prepared in methanol at the concentration of 2000 mg L⁻¹ for benzene, and 1000 mg L⁻¹ for toluene, ethylbenzene, *o*-xylene and (*m* + *p*)-xylenes. The solutions were stored in refrigerator. An intermediary standard solution at the concentration of 10–20 mg L⁻¹ was prepared by diluting the stock standard solutions in pure water. More diluted working solutions were prepared daily by diluting the intermediary standard solution with water. Working solution used to optimize the experimental parameters was prepared daily at the concentration of 50–100 µg L⁻¹ in water. Pure water was prepared by OES (Overseas Equipment & Services) water purification system (OK, USA). Polydimethylsiloxane SPME fiber (PDMS, 100 µm thickness) and SPME fiber holder assembly was purchased from Supelco (Bellefonte, PA, USA). A digital magnetic stirrer (MR 3000D) from Heidolph (Kelheim, Germany) was used for the stirring of the solutions. The high-purity copper wire (0.28 mm O.D.) was used as the substrate for the deposition of Cu foam. River and wastewater samples were collected in amber-glass bottles without headspace. The real samples were stored in the refrigerator until their analysis.

2.2. Instrumentation

The analysis of the analytes was carried out using a SP-3420 gas chromatograph equipped with a split/splitless injector and a flame ionization detector (BFRL, Beijing, China). The injection port was equipped with a low volume insert designed for analysis by SPME (Restek Bellefonte, PA, USA). Nitrogen gas (99.999%) at a head pressure of 100 kPa was used as carrier gas. The detector gasses flow rate were 300 mL min⁻¹ of air, 30 mL min⁻¹ of hydrogen and 25 mL min⁻¹ of nitrogen as make-up gas. Separation was carried out with a BP5 fused silica capillary column, 30 m × 0.25 mm, with a 0.25 µm stationary phase thickness (SGE, Australia). The injector and detector temperatures were set at 260 °C and 280 °C, respectively. The column temperature was held at 50 °C for 4 min and then programmed at 20 °C min⁻¹ to a final temperature of 240 °C for 3 min.

The electrodeposition of copper foam coating was performed using an Autolab electrochemical system Model-PGSTAT 12 and FRA2 boards (Eco Chemie B. V., Utrecht, Netherlands). The system was run on a PC using GPES and FRA 4.9 software. The morphology of the fiber coating was observed using a HITACHI S-4160 (Tokyo, Japan) field emission scanning electron microscope (FE-SEM) operated at 30 kV.

Characterization in terms of specific surface area, pore volume, and pore diameter of the prepared foam was determined by N₂ adsorption at 77 K with surface area and pore size analyzer (model PHS-1020) using the Brunauer–Emmett–Teller (BET) method.

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