Journal of Chromatography A, 1300 (2013) 104–111

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

A solid phase microextraction coating based on ionic liquid sol–gel technique for determination of benzene, toluene, ethylbenzene and *o*-xylene in water samples using gas chromatography flame ionization detector

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ARTICLE INFO

Article history:
Available online 26 March 2013

Keywords:
Solid-phase microextraction
Ionic liquid
Sol–gel technique
Gas chromatography
BTEX

ABSTRACT

Ionic liquid mediated sol–gel sorbents for head-space solid phase microextraction (HS-SPME) were developed for the extraction of benzene, toluene, ethylbenzene and *o*-xylene (BTEX) compounds from water samples in ultra-trace levels. The analytes were subsequently analyzed with gas chromatography coupled to flame ionization detector (GC-FID). Three different coating fibers were prepared including: poly(dimethylsiloxane) (PDMS), coating prepared from poly(dimethylsiloxane) in the presence of ionic liquid as co-solvent and conditioned at a higher temperature than decomposition temperature of ionic liquid (PDMS-IL-HT) and coating prepared from poly(dimethylsiloxane) in the presence of ionic liquid as co-solvent and conditioned at a lower temperature than decomposition temperature of ionic liquid (PDMS-IL-LT). Prepared fibers demonstrate many advantages such as high thermal and chemical stabilities due to the chemical bonding of the coatings with the silanol groups on the fused-silica surface fiber. These fibers have shown long life time up to 180 extractions. The scanning electron micrographs of the fibers surfaces revealed that addition of ionic liquid into the sol solution during the sol–gel process increases the fiber coating thickness, affects the form of fiber structure and also leaves high pores in the fiber surface that cause high surface area and therefore increases sample capacity of the fibers. The important parameters that affect the extraction efficiency are desorption temperature and time, sample volume, extraction temperature, extraction time, stirring speed and salt effect. Therefore these factors were investigated and optimized. Under optimal conditions, the dynamic linear range with PDMS-IL-HT, PDMS and PDMS-IL-LT fibers were 0.3–200,000; 50–200,000 and 170–150,000 pg mL^{-1} and the detection limits (S/N = 3) were 0.1–2 and 15–200 and 50–500 pg mL^{-1}, and limit of quantifications (S/N = 10) were 0.3–8 and 50–700 and 170–1800, respectively. The relative standard deviations (RSD) for one fiber (repeatability) (*n* = 5), were obtained from 3.1 up to 5.4% and between fibers or batch to batch (reproducibility) (*n* = 3) in the range of 3.8–8.5% for three fibers. The developed method was successfully applied to the real water samples while the relative recovery percentages obtained for the spiked water samples at 20 pg mL^{-1} were from 91.2 to 103.3%.

1. Introduction

Benzene, toluene, ethylbenzene and xylene (*m*-, *p*- and *o*-xylene) which are named BTEX, are important industrial chemicals. BTEX (especially benzene) are hazardous carcinogenic and neurotoxic compounds, and are classified as priority pollutants by the US Environmental Protection Agency (EPA). Some of the relevant sources of these compounds include tobacco smoking; vehicular traffic; industrial paints, adhesives and glues [1–3].

Traditional methods of sample preparation have high risk for loss of analytes and are typically time consuming because they employ multi-step procedures. They also use extensive amounts of organic solvents. A special attention is focused on the techniques which considerably reduce or completely eliminate the use of organic solvents. Such techniques decrease the environment pollution and cost of analysis [4].

SPME was introduced by Pawliszyn and co-workers in the early 1990s [5]. This technique employs a small volume of polymeric extracting phase, which is used to isolate and to concentrate target analytes of interest from complex samples [6]. SPME is a solvent-free technique that has many advantages over conventional extraction methods including small sample-amount requirements, automation capability, high analysis speed, simplicity and ease

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http://dx.doi.org/10.1016/j.chroma.2013.03.039

of operation. It is a solventless microextraction method which makes it more environmentally friendly, and also simplifies the overall sample preparation procedure by minimizing the number of required steps thus enabling it to achieve widespread use in analytical separation [7–12].

Commercial SPME fibers such as PDMS, polyacrylate (PA), carbowax/divinylbenzene (CW/DVB), poly-dimethylsiloxane/divinylbenzene (PDMS/DVB), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and polydimethylsiloxane/carboxen (PDMS/carboxen) are available [13]. Although the application of SPME fibers is being increased, but the presence of some important drawbacks such as relatively low operating temperature, low chemical and mechanical stability which cause that results in fiber breakage and stripping of coatings, and also their expensive cost have produced some difficulties in their applications [14].

The lack of proper chemical bonding of the stationary phase coating with the fiber surface seems to be responsible for some of these drawbacks such as low thermal and chemical stability. Sol–gel coating technology has shown to be able to overcome these problems. The first description of sol–gel technology applied for preparation of SPME fibers was presented by Malik and co-workers in 1997 [15]. Since then, sol–gel technology has emerged as the most popular approach in preparing novel SPME coatings.

Sol–gel chemistry offers an effective methodology for the synthesis of inorganic polymer and organic–inorganic hybrid materials under extraordinarily mild thermal conditions (typically at room temperature). Since sol–gel processes can be used to obtain products of various shapes, sizes, and formats; sol–gel technology has found ever-increasing applications in a diverse range of scientific and engineering fields [16].

The porous structure of the sol–gel coating offers a high surface area; allowing high extraction efficiency. One method that enhances the sample capacity is to create the sol–gel coatings with porous morphology using porogenic agent(s) in the sol solution. Organic solvents, polymers, surfactants, micelles and inorganic salts are used in sol–gel technology as porogenic agents [17]. Recently, ionic liquids (ILs) have been used as porogens for sol–gel materials [18–20].

ILs are organic salts which consist largely of organic cations paired with organic or inorganic anions. In recent years, ionic liquids have gained considerable attention in the analytical chemistry community due to their unique physical and chemical properties which include high thermal stability, low vapor pressures, and their ability to be recycled [21,22]. ILs have found many applications in a number of areas in separation chemistry such as chromatographic and extraction methods [23–29]. There are some useful reviews about application of ILs in analytical chemistry [30–32]. ILs can have significant effects on the porous structure of sol–gel materials [33–35] and reducing the cracking and shrinking [36,37] during solvent evaporation from the sol–gel pores. Malik and co-workers introduced IL-mediated sol–gel coatings for capillary microextraction [38,39].

In this work, for the first time, we developed a new SPME fiber through preparation of IL-mediated sol–gel coatings technology. During the sol–gel reactions, the created ionic liquid mediated sol–gel became chemically bonded to the fused-silica fiber. The developed coating was then used for the determination of BTEX in real water samples with GC-FID.

2. Experimental

2.1. Reagents and materials

Hydroxy-terminated poly(dimethylsiloxane) (PDMS) was purchased from Flucka (Buchs, Switzerland); methyltrimethoxysilane (MTMOS) (synthesis grade), trifluoro-acetic acid (TFA) (99%) and poly(methylhydrosiloxane) (PMHS) were purchased from Merck (Darmstadt, Germany).

Analytical reagents grade methanol, methylene chloride, benzene, toluene, ethylbenzene and *o*-xylene were also purchased from Merck (Darmstadt, Germany).

1-Hexyl-3-methyl-imidazolium hexafluorophosphate C_6MIM] [PF_6] was from Ionic Liquids Technologies (Denzlingen, Germany).

2.2. Instrumentation

A Chrompack CP9001 (Middelburg, the Netherlands) GC equipped with a split/splitless injector and flame ionization detector (FID) was utilized for analysis of BTEX compounds. Helium (99.999%, Sabalan Co., Tehran, Iran) was used as the carrier gas. In order to focus the analytes at the head of the column to reduce the band broadening, the carrier gas flow was set at 0.2 mL min^{-1} for 20 s and then increased up to 1 mL min^{-1} and was kept constant until the end of GC run time. The flow rate of air (99.99%, Sabalan Co., Tehran, Iran) as oxidant for FID was 250 mL min^{-1} and the flow rate of hydrogen (99.99%, Sabalan Co., Tehran, Iran) (as FID fuel) was 25 mL min^{-1}.

Separations were conducted using a CP-Sil 24 CB (50% phenyl, 50% dimethylsiloxane) capillary column, WCOT Fused silica, 30 m × 0.32 mm ID with 0.25 μm stationary film thickness (Chrompack, Middelburg, The Netherlands). Column temperature program was as follows: 3 min in 40 °C and then increased to 100 °C at the rate of 10 °C min^{-1}, then to 180 °C at the rate of 20 °C min^{-1} and held at this temperature for 1 min. The injection port temperature was set at 250 °C and desorption of analytes from the fiber surface was carried out in the splitless mode for 20 s, plus 5 additional minutes with the split valve on, for complete removal of analytes. The FID temperature was held at 260 °C.

An ultrasonic bath (Branson 1510, Branson Ultrasonics Co., Danbury, CT), was employed at a frequency of 42 kHz to mix various solution ingredients in sol–gel process. Sample stirring and heating during the extraction step, was carried out with a VELP Scientifica heating magnetic stirrer, model ARE (Milano, Italy). A scanning electron microscope (SEM) (LEO, model 1450VP, Germany) was employed to study the surface of sol–gel fiber coating. Manual injection of the fibers was performed by a home-made fiber holder.

2.3. Fiber pretreatment

An used GC capillary column was cut with a cutter device in 3 cm long. Polyamide protective layer of 1 cm segment of this 3 cm long fused silica fiber was removed by burning on the burner flame. Afterward bare fiber segment was dipped into 1 M NaOH solution for 1 h, to expose the maximum silanol groups on the surface, then it was rinsed with water and placed in 0.1 M HCl solution for 30 min to neutralize the excess of NaOH. Thereafter it was washed again with water and dried.

2.4. Sol–gel coatings preparation

In this work, three different coated fibers which were prepared are PDMS, PDMS-IL-HT and PDMS-IL-LT fibers. The names and chemical structures of sol solution ingredients used to prepare these three sol–gel coatings are shown in Table 1.

2.4.1. Preparation of PDMS fiber

The sol solution was prepared as follows: 100 mg of PDMS was dissolved in 150 μL of methylene chloride in a clean eppendorf tube using ultrasonic agitation for 5 min. Then 100 μL of MTMOS and 30 μL PMHS were added and mixed thoroughly for 5 min. A