Single-step reinforced microextraction of polycyclic aromatic hydrocarbons from soil samples using an inside needle capillary adsorption trap with electropolymorized aniline/multi-walled carbon nanotube sorbent

Ali Reza Ghiasvand *, Fatemeh Yazdankhah

Department of Chemistry, Lorestan University, Khoramabad, Iran

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ABSTRACT

A polyaniline/multi-wall carbon nanotubes (PANI/MWCNT) composite was electrodeposited on the interior surface of a platinumized stainless steel capillary needle and used to prepare an inside needle capillary adsorption trap (INCAT) device. The platinumization expanded the interior adsorbing surface of the needle and made it more porous and cohesive for nanocomposite film. The nanocomposite was characterized using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The fabricated INCAT was fixed into a cooling capsule to fabricate a cooling-assisted INCAT (CA-INCAT) system. The CA-INCAT device was used to extract polycyclic aromatic hydrocarbons (PAHs) from solid samples followed by gas chromatography-flame ionization detection (GC-FID) determination. To obtain the best extraction efficiency, the important experimental variables were studied and optimized. Under the optimal conditions, the limits of detection (LODs) for the studied PAHs were in the range of 0.002–0.02 ng g⁻¹. Linear dynamic ranges (LDRs) for the calibration curves were found to be 0.1–30,000 ng g⁻¹. Relative standard deviations (RSDs%) for six replicated analysis of 1 ng g⁻¹ PAHs were obtained 7.7–11%. The CA-INCAT-GC-FID method was successfully applied for the extraction and determination of PAHs in contaminated soil samples. The results were in agreement with those obtained by a validated ultrasound-assisted solvent extraction (UA-SE) method.

1. Introduction

Solid-phase microextraction (SPME), which was introduced by Pawliszyn in 1989, is one of the best known modern sample preparation methods [1]. Numerous applications, in different fields, have demonstrated that SPME is a fast, simple, effective, and easily automated solvent-free sample preparation strategy [2]. Despite the mentioned advantages, SPME fibers are fragile and expensive, have low capacity and limited to a few number of extraction phases [3]. To compensate these drawbacks and further enhancement the extraction efficiency, different needle-based SPME techniques include needle trap device (NTD) [4], in-needle extraction (INE) [5], in-tube extraction (ITE) [6], solid-phase dynamic extraction (SPDE) [7], fiber-in-needle solid-phase microextraction (FIN-SPME) [8], inside needle capillary adsorption trap (INCAT) [9] and microextraction in a packed syringe (MEPS) [10] were developed. In MEPS, the sorbents and extraction conditions are almost similar to solid-phase extraction (SPE), but its sorbent bed is packed into the tip of a microsyringe, which allows for low volume sample handling.

Among these needle-based techniques, INCAT is an inexpensive, robust and reusable configuration of SPME which possesses a larger extraction capacity and is considered as a powerful microextraction and preconcentration method. It is a hollow needle which encompasses either an internal sorbent film or a short length of GC capillary column placed inside it. The extraction step may be performed in a gaseous or liquid phase or the headspace of a liquid or solid sample, by flowing the gas or liquid through the INCAT device with a pump or syringe (active sampling), or by diffusion (passive sampling). So, the analytes present in the sample are sorbed onto the deposited coating, inside the internal surface of needle. Then, the desorption step performs by placing the INCAT device into the hot injection port of a GC to desorb the analytes. Despite the outstanding advantages of INCAT, compared to the other needle-based methods, it has received much less attention by scientists, possibly because of the physical problems in the inner-surface coating of the needle. For this reason, few of sorbents have been used in its preparation, include activated carbon [11], a piece of GC capillary column [9], polydimethylsiloxane [12], polypak Q [13], polypropylene [14], and molecularly imprinted polymer [15]. Based on our knowledge, the only nano compound that has been used in preparation of INCAT is polyaniline/hexagonally ordered silica nanocomposite [16].

The nanosorbents coatings can adsorb/desorb analytes more efficiently, due to their uniquely ordered-structure and large surface area [17]. Among these nanosorbents, the composite of polyaniline (PANI) coated with multiwall carbon nanotubes (MWCNT) has attracted higher interest, due to its special physiochemical features [18]. Only or in combination with the nanocarbon sorbents, PANI has
been deposited on different substrates such as stainless steel wire and platinum fiber to prepare the microextraction devices [19]. PANI and its nanocomposites are generally deposited on the substrates by the sol-gel process [20] or the electrochemical deposition (EPD) method [21]. EPD has comparative advantages over other coating techniques. It is demonstrated that EPD is scalable, where the films are deposited onto the substrates as large as the automotive bodies and as small as the nanoscale electrodes. The characteristics of the EPD cast film can be tuned to targeted values by manipulating the variable parameters such as the operating DC voltage, frequency, preparation method of the templates and chemistry of the nanocrystal surface. These combined features make EPD a flexible and powerful deposition procedure to produce robust and stable nanoparticle thin films [22].

On the other hand, the hand-made SPME fiber coating and INCAT deposited films are often unstable and breakable and easily peeled by the physical contact or organic solvents, because of the smooth surfaces of the bed and lack of proper adhesion between the substrate and the coating film. This defect was compensated in our previous experience by platinitizing the surface of stainless steel SPME fiber to attain a cohesive, porous and large surface area fiber base [23]. Accordingly, the fiber bed became porous, large surface area and remarkably resistant to chemical and mechanical stresses. Accordingly, in this research, we tried to make the interior surface of a stainless steel needle cohesive and porous by platinitization to obtain an INCAT, with mechanically strength, chemically resistant and more sorptive surface, for its deposited film. Thus, for the first time, the interior surface of an INCAT device was platinitized using an optimized version of a previously reported EPD procedure [24]. Afterward, the platinitized interior surface of the INCAT was coated with a PANI/MWCNT film using a proper flow-through in-situ electropolymerization method. In this way, by depositing the mechanically and thermally stable and high extraction efficiency PANI/MWCNT coating on the platinitized interior surface of the stainless steel needle, a powerful, robust, durable, and effective INCAT device was prepared for the extraction of volatile organic compounds (VOCs).

Generally, the analysis of natural solid samples such as soil, sediment and plant samples is difficult, due to tight attaching of analytes to the active sites present in their complicated matrices. For this purpose, the analytes must be released from their native sites, diffuse to the headspace and concentrated on the extraction phase [25,26]. The most effective solution for this problem is simultaneously increasing temperature of the sample matrix and lowering temperature of the extraction phase, which is known as cooling-assisted microextraction (CA-ME) [27]. Therefore, to enhance the extraction efficiency of the INCAT device, it was coupled to a cooling-assisted system, which its reliability has been demonstrated previously [28]. Based on a deep literature review, this is the first cooling-assisted INCAT (CA-INCAT) system, which utilizes the capabilities and benefits of INCAT, PANI/MWCNT nanocomposite, and CA-ME. The CA-INCAT setup was then coupled to gas chromatography-flame ionization detection (GC-FID) and used to extract and determine polycyclic aromatic hydrocarbons (PAHs) from polluted soil samples.

2. Experimental

2.1. Reagents and supplies

Extra pure aniline (99.5%), analytical reagent grade sodium dodecyl sulfate (SDS) and potassium hexachloroplatinate (IV) (K₂PtCl₆) were purchased from Merck (Darmstadt, Germany). All acids and bases and all of the used organic solvents were of the analytical reagent grade and provided by Merck. Multi-walled carbon nanotube (MWCNT) with purity higher than 95% (10–20 nm O.D., 5–10 nm I.D. and 10–30 μm length) was purchased from Plasma Chem (Berlin, Germany). Naphthalene (Nap), fluorene (Flr), phenanthrene (Phe), fluoranthene (Flt), and pyrene (Pyr), all of purity >99.0%, were purchased from Sigma Aldrich (Germany). A stock solution (1000 μg mL⁻¹) was prepared by dissolving appropriate amounts of five PAHs in methanol. The working standard solutions were prepared weekly by diluting the standard stock solution. All PAHs stock and working solutions were stored at 4 °C.

2.2. Instruments

Gas chromatographic separations and determinations were carried out using a Shimadzu GC-2010 Plus AF gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a split/splitless injector (SPL-2010 Plus) system and a flame ionization detector (FID-2010 Plus). It was run with the GC solution software (version 2.4). The separations were performed using a HT-5 fused-silica capillary column (15 m × 0.32 mm × 0.5 μm). The stainless steel needle of 21-Gauge (12 cm L, 0.7 mm I.D., 0.9 mm O.D. with a side hole) was used for fabrication of the INCAT device. Heating the samples was carried out using a Heidolph MR 3001-K magnetic heater-stirrer (Kelheim, Germany), A 1-μL microsyringe (Hamilton, Nevada, USA) was used for the GC direct sample injection. The CA-INCAT extractions were conducted using 40 mL sample vials with plastic crimp caps and PTFE-coated silicone seata (Supelco, USA). Fourier transform infrared spectra were recorded by an FT-IR 8400 spectrometer (Shimadzu, Japan) in the transmittance mode, and employed to characterize the functional groups of the PANI/MWCNT nanocomposite. A VEGA-TESCAN scanning electron microscope (SEM CM120, Czech) was used to investigate the morphology of the nanocomposite coating. The cooling-assisted setup was fabricated as described previously [29,30]. A peristaltic pump (FLEXIFLO INTERNAL PUMP, Ross Products, Columbus, OH, USA) was used for aspirating the headspace into the INCAT device.

2.3. GC-FID separation and determination of PAHs

To achieve the best separation and determination conditions of the PAHs, the GC-FID temperature program was optimized. The oven temperature program was started by remaining at 100 °C for 1 min. Then, temperature was raised to 240 °C with a rate of 20 °C min⁻¹ and held constant for 2 min. Finally, the temperature was raised (30 °C min⁻¹) to 280 °C and held constant for 3 min. Both the injector and detector of the GC system were set at 280 °C and runs conducted in the split mode (split ratio of 1/10). Nitrogen (99.999% pure) was used as the carrier gas at a flow rate of 1 mL min⁻¹. The flow rates of air, hydrogen (as FID gases), and makeup gases were set at 300, 30, and 30 mL min⁻¹, respectively. To obtain the retention times and standard calibration curves, several standard solutions of the PAHs with different concentrations were prepared and 1 μL of each of them was directly injected into the GC-FID system in the split mode (with a split ratio of 1/10). Good calibrations (R² > 0.99) were obtained over the range 0.5–50 μg mL⁻¹ for the five studied PAHs.

2.4. Synthesis of PANI/MWCNT nanocomposite and preparation of INCAT

The platinitization of the interior surface of INCAT stainless steel needle was conducted through a modified version of a previously published method [23,24]. Afterward, the simultaneous synthesis of