



Cooling/heating-assisted headspace solid-phase microextraction of polycyclic aromatic hydrocarbons from contaminated soils



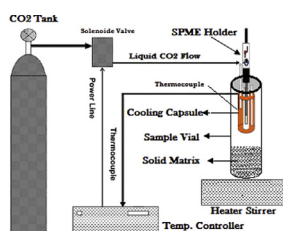
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HIGHLIGHTS

- A novel, effective and low-cost cooling/heating assisted solid-phase microextraction (CHA-SPME) device was introduced.
- It can simultaneously cool the extraction phase and heat the sample matrix in SPME (handmade and commercial fibers), LPME, NTD, and INCAT.
- Compared to conventional methods, its extraction time is too much shorter and its efficiency is higher.
- It can be utilized to analyze complicated solid samples, with no need to sample pretreatment.

GRAPHICAL ABSTRACT



The proposed CHA-HS-SPME device

ARTICLE INFO

Article history:

Received 17 July 2015

Received in revised form

15 October 2015

Accepted 17 October 2015

Available online 26 October 2015

Keywords:

Cooling/heating-assisted solid-phase microextraction
Polycyclic aromatic hydrocarbons
Contaminated soil

ABSTRACT

A simple, low-cost, and effective cooling/heating-assisted headspace solid-phase microextraction (CHA-HS-SPME) device, capable of direct cooling the fiber to low temperatures and simultaneous heating the sample matrix to high temperatures, was fabricated and evaluated. It was able to cool down the commercial and handmade fibers for the effective tapping of volatile and semi-volatile species in the headspace of complex solid matrices, with minimal manipulation compared with conventional SPME. The CHA-HS-SPME system can create large temperature gaps (up to 200 °C) between the fiber and the sample matrix, because the cooling process is directly applied onto the fiber.

Different effective experimental parameters for the fabrication of the CHA-HS-SPME device as well as for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs) from solid samples were evaluated and optimized. The proposed device coupled to GC-FID was successfully applied for the extraction and determination of PAHs in contaminated soils without any sample pretreatment step. Good agreement was observed between the results obtained by the proposed CHA-HS-SPME-GC-FID method and those achieved by validated method.

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1. Introduction

Solid-phase microextraction (SPME) was introduced by Pawliszyn [1] to overcome the drawbacks associated with conventional extraction methods like liquid-liquid extraction (LLE), solid-phase extraction (SPE), and conventional thermal desorption. SPME

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reduced the steps and time of analytical determinations and opened up a new horizon for analysts. Consequently, many efforts have been made to improve its modes [2–5] and applications [6,7]. However, due to complications with its practical manipulation, limited research has focused on improving the performance of the basic primary modes of SPME [8,9]. Nevertheless, the proposed designs and developments not only were expensive and complicated, but also could not significantly improve the abilities and extraction efficiency of SPME [10–12]. One of the few succeeded endeavors made to raise the efficiency of SPME was cold-fiber solid-phase microextraction (CF-SPME) [8].

On the one hand, a serious challenge in environmental, biological and nutritional solid matrices is trapping and extracting volatile compounds. Direct thermal desorption (DTD) [13], static head-space (SHS) gas chromatography [14], head-space sorptive extraction (HSSE) [15], and head-space solid-phase microextraction (HS-SPME) [16,17] are some general alternatives to conventional extraction methods for this purpose. HS-SPME is not as sensitive as DTD, but has a better sensitivity than SHS. Thus, for effective extraction of volatiles from solid matrices, improving the sensitivity of HS-SPME is a major concern [18]. The main challenges in HS-SPME are collecting volatiles onto microextraction phase and releasing low volatile analytes from their native matrix into headspace, especially in complicated solid matrices. The most effective solution to release analytes from their matrix is thermal desorption, which provides enough kinetic energy and reinforces molecules to escape from their matrix, enhances their mass transfer to pass through the matrix, and increases their concentration in headspace by increasing vapor pressure. However, due to the exothermic character of absorption, increasing temperature of the sample can conversely decrease trapping the analytes onto fiber's coating. Indeed, temperature has a bilateral effect. It increases extraction efficiency by increasing concentration in the headspace, but decreases the tendency of coating to the absorbed analytes. Therefore, in the temperature profile of any headspace SPME sampling, there are usually an ascending part and a descending region with an optimum temperature between them [19]. This optimal temperature is not usually high enough for significant improvement in the extraction efficiency of volatiles, especially in solid matrices with their analytes firmly attached. This effect may be compensated by creating a temperature gap between fiber's coating and headspace, to simultaneously increase distribution coefficients of equilibria between sample matrix and headspace as well as between headspace and fiber coating. This strategy lets contaminated samples, such as soils and sediments, be directly analyzed with minimal manipulation and in a single step.

The first promotion in SPME efficiency was made with the internally-cooled solid-phase microextraction (IC-SPME) device introduced by Zhang et al. in 1995 [8]. The IC-SPME device was successfully examined for the quantitative extraction of benzene, toluene, ethylbenzene, and xylene (BTEX) in clay soil samples. It used a Hamilton 1710RN gastight syringe barrel as the SPME device with changing its plunger and needle to 19- and 17-gauge stainless steel tubing. Moreover, a silica capillary tube was used as fiber and a piece of polydimethylsiloxane (PDMS) liquid polymer tubing as fiber's coating. Anyhow, the fiber was fragile and its coating was bound to PDMS as the only applicable fiber's coating. In general, using the IC-SPME device was tedious. However, it was a starting point to improve the microextraction methods by the cooling process. This project remained inactive until 2006 when a modified version of the previous design named cold-fiber headspace solid-phase microextraction (CF-HS-SPME) device was introduced [20]. The new full-automated miniaturized design (i.e., CF-HS-SPME), which accommodated the fiber into an 18-gauge stainless steel needle, was robust and its fiber was reproducibly used for more than

a dozen injections without any coating stripping or damage. The CF-HS-SPME design used a 33-gauge stainless steel tubing to deliver liquid carbon dioxide for cooling the fiber. This combination was rugged and easy to use. Moreover, a handmade restrictor was made and used for the adjustable and precise control of flow rate and, consequently, coating's temperature at smaller intervals. Unlike the previous system, application of an adjusting tube prevented the fiber's coating to be stripped in contact with the edges of a needle during movement inside it. The proposed CF-HS-SPME device was mounted on a CTC CombiPAL autosampler arm and full-automatically used. It is worth noting that, unlike conventional SPME, the temperature profile does not have the descending part. In other words, higher temperatures can be used if the sample situation allows. This system was successfully applied directly to trap and extract PAHs from sand and sediment samples, with minimal manipulation. Although the CF-SPME system was introduced to be better than the previous one (IC-SPME), it has its own problems. For example, its construction is difficult and its use is troublesome. The proposed CF-HS-SPME device was then validated with the back equilibration of BETX and PAHs preloaded onto the fiber in air [21].

In a different research, the proposed full-automatic CF-HS-SPME device, coupled to a gas chromatography time-of-flight mass spectrometric detection (GC-TOF-MS), was directly applied to determine the flavor profile of fragrant rice samples in 2007 [22]. The results showed that uncooked rice samples can be successfully analyzed even as dry kernels. These results established that the automated CF-HS-SPME-GC-MS system provides a powerful approach to rapidly profiling the flavor components of foods without manipulation of their samples, which is valuable for agricultural and commercial purposes. Afterwards, the proposed CF-SPME system was used by researchers for the analysis of various analytes in different conditions [23–29]. However, despite all the previously mentioned benefits, there are some limitations associated with this new device. Its syringe construction is really tedious and the exact control of temperature in a narrow preset range is still too difficult. Although these drawbacks can be addressed by further modification of the system, there is still a need to develop a compact system with fewer parts, compatible to use different fiber's coatings, applicable to handmade fibers, easier construction process and, specially, applicability for proper field sampling. Thermoelectric cooler (TEC), used in miniaturized analytical instruments [30], is a proper alternative cooling tool for CF-SPME. For instance, TEC has low cost, small size, low weight, no moving parts, and can precisely control the temperature. However, the most important requirement to achieve higher efficiencies is the ability to transfer heat directly to the extraction phase.

The first use of TEC technology in SPME was developed by Hosseinzadeh et al. [10]. In this work, a new CF-SPME device was designed and constructed based on copper rod coated with PDMS as the SPME fiber, and a three-stage TEC for cooling the fiber. The study of TEC–CF–SPME was continued by Banitaba et al. in 2014 [31]. In this research, poly (3, 4-ethylenedioxythiophene) and graphene oxide nanocomposite were electrochemically coated on gold wire as SPME fiber. Cooling the SPME fiber was conducted using a commercial TEC instrument. The proposed TEC–CF–HS-SPME, coupled to GC-FID, was successfully used to extract PAHs from seawater samples. However, regardless of sample types, the obtained LDRs and LODs for PAHs are not comparable with those reported by CF-HS-SPME using an internally cooled fiber [20]. Moreover, despite the benefits associated with the proposed TEC–CF–SPME setup, it lacks proper efficiency when high temperature gaps are applied between the sample matrix and fiber's coating. This fact is revealed from the extraction temperature profile, which is similar to that of the conventional SPME [32], in which fiber and sample are both at the same temperature. The main disadvantage of the

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