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In-syringe solid-phase extraction for on-site sampling of pyrethroids in environmental water samples

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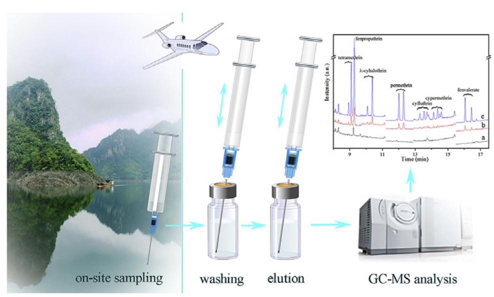
HIGHLIGHTS

- Hierarchical porous graphene aerogel was synthetized and used as the sorbent in in-syringe SPE.
- The proposed in-syringe SPE method was applied for on-site sampling of pyrethroids in environmental water samples.
- The pyrethroids could be completely extracted during one aspirating/dispensing cycle.
- The pyrethroids could be stable on the sorbent for at least 72 h and would not be affected by the sample pH.

GRAPHICAL ABSTRACT



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ABSTRACT

On-site sampling is an analytical approach that can ensure the accuracy of monitoring data and enhance the effectiveness of environmental protection measures. In the present work, an in-syringe solid-phase extraction (SPE) device was designed for on-site sampling of trace contaminants in environmental water samples followed by gas chromatography-mass spectrometry (GC-MS) analysis. Template assisted freeze casting followed by hydrazine vapor reduction approach was used to synthesize a hierarchical porous graphene aerogel (HPGA), which was used as the sorbent in the in-syringe SPE device. Environmental degradable pyrethroids were selected as the model analytes. Owing to the large specific surface area and hydrophobicity of HPGA, the target molecules could be completely extracted during one aspirating/dispensing cycle. The analytes were stable on the sorbent for at least 72 h when the device was stored under airtight and light-free conditions, and were not affected by the pH value of sample solution. All results demonstrated that the device could meet the requirements of on-site sampling. For practical application, the limits of detection were found to be in the range of 0.012–0.11 ng mL^{-1} under the optimized conditions, and satisfactory recoveries in the range of 65.7–105.9% were obtained for the analysis of real samples. The results of this study demonstrate the immense potential of HPGA for the

Abbreviations: SPE, solid-phase extraction; GA, graphene aerogel; GO, graphene oxide; HPGA, hierarchical porous graphene aerogel; PS, polystyrene microspheres.

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enrichment of trace environmental pollutants, and meanwhile promote the application of the in-syringe SPE technique as a promising candidate for on-site sampling.

1. Introduction

Environmental issues have long been of immense concern to the wellbeing and development of humankind, thus environmental protection remains a long-term and arduous task. The quality control of environmental monitoring is of great significance to ensure the accuracy of monitoring data and improve the effectiveness of environmental protection measures. Recently, there has been increasing interest in environmental monitoring among analytical chemistry scientists [1–3]. However, routine laboratory analysis involves multiple steps, including sample collection, sample storage, transportation, sample treatment and finally instrumental analysis. During this process, the loss and degradation of the analytes is inevitable, especially in sample storage and transportation [4]. Therefore, on-site analysis or on-site sampling/laboratory analysis are proposed to obtain more quickly available, accurate and representative analytical data. In general, on-site analysis requires suitable sample preparation approaches and portable instruments with limited sensitivity, which are sometimes not feasible.

Significant efforts in analytical chemistry are currently devoted to the development of suitable methods to facilitate on-site sampling [5,6]. Since the targets transferred into the extraction phase show improved stability as compared to those in the natural matrix. Thus, a higher requirement has been put forward to the sampling devices [6]. On the basis of actual application requirements, the suitable sampling devices for on-site sampling are supposed to exhibit the following features. Firstly, sampling sites are generally remote areas with no access to laboratory facilities, therefore, the devices should be miniaturized and portable so that they can be conveniently taken to the sampling sites. Secondly, simple and reliable operation should be available on account of the sampling time should not be used any longer than necessary. Additionally, the production of the device should be uncomplicated and inexpensive. Solid-phase microextraction (SPME) has been certified as an effective sample preparation method for on-site sampling to address these issues [7,8]. It is a solvent-free technique with simple operation and high enrichment factors which integrates sampling, extraction and enrichment into a single step [9,10]. However, the longer equilibrium time together with the high costs involved confine the application of SPME in considerable routine on-site sampling.

Recently, many different types of sample preparation methods based on SPE technique have been exploited to meet different application requirements, such as magnetic (or dispersive) solid-phase extraction (SPE) [11–13], micro SPE [14,15], microextraction by packed sorbent [16,17], in-syringe (dispersive) SPE [18–21], and so on. Among these techniques, in-syringe SPE is a kind of sample preparation technique that has made great progress in recent years. In this format, the sorbent is packed in the nozzle of disposable syringe which is kept fixed by degreasing cotton or mesh plates. The loading and eluting processes are carried out by aspirating and dispensing into the sample solution or eluent. This method exhibits significant features, such as miniaturization and portability, simple and reliable operation as well as cost-efficiency, which could lay the foundation of in-syringe SPE for a wide range of practical applications. Feng and co-workers developed various methods for bioanalysis based on different kinds of materials [22–25]. In their recent work, a carboxyl cotton chelator-titanium (IV) fibers based in-syringe SPE method was applied for the specific capture of phosphopeptides from multiple biological samples [22]. This method greatly simplified the entire process of enrichment and showed rapid convenient procedure and excellent performance. In the light of the advantages mentioned above, the developed in-syringe SPE method was expected to realize its own value for on-site sampling in environmental water sample analysis. However, to the best of our knowledge, its application for on-site sampling is hitherto unreported.

Graphene and its composite materials have been extensively studied in separation science [26–30] in recent years. Three dimensional porous graphene materials (3DPGM), a novel kind of functional materials, not only possess the inherent physicochemical properties of graphene, but also exhibit many other interesting features. For the application of adsorption and separation, its feature of large surface area enhances the opportunity to contact target molecules, and the characteristic of well-defined porous structure is conducive to improve the mass transfer efficiency. Based on the above advantages, 3DPGM has been investigated in adsorption and preconcentration of contaminants in different environmental matrix in our previous work [31–33]. In this study, we report a hierarchical porous graphene aerogel (HPGA) based in-syringe SPE method for on-site sampling of contaminants in environmental water samples. The HPGA was synthesized in-situ in the nozzle through template assisted freeze casting followed by hydrazine vapor reduction and toluene washing. Pyrethroids pesticides were selected as model analytes to evaluate the SPE performance of the designed device. On-site loading of samples was performed through aspirating and dispensing the sample solutions, and the subsequent elution and analysis steps were also explored in the developed method. A series of parameters affecting the extraction efficiency of pyrethroids, in the process of on-site sampling and elution, were carefully optimized to obtain the optimum extraction performance of the HPGA. Finally, the proposed method was applied to the on-site sampling of real water samples.

2. Experimental

2.1. Chemicals and materials

Expanded graphite powder (100 mesh) was purchased from Xinghe Graphite Co., Ltd. (Qingdao, China). The chemicals used for the synthesis of graphite oxide were supplied by Beijing Chemical Works (Beijing, China). Polystyrene microspheres (PS, 5 wt %, 500 nm particle diameter) were obtained from Janus New Materials Co., Ltd. (Nanjing, China). The organic reagents used for chromatographic analysis were of HPLC grade and purchased from Amethyst Chemicals (J&K Scientific, Beijing, China). The mesh plate (4.0 mm × 1.6 mm) were purchased from Biocomma Biotech Co. Ltd. (Shenzhen, China). The nozzles were taken from disposable syringes and washed with acetone thoroughly by ultrasound, and dried at room temperature. The barrel used for SPE experiments was all-glass material and obtained from Xinyue Glass Instrument Co. Ltd. (Changzhou, China).

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