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Advances in different configurations of solid-phase microextraction and their applications in food and environmental analysis

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A B S T R A C T

Major objectives in research for food and environmental samples include improving robustness, sensitivity, selectivity, and extraction efficiency for polar organic compounds, avoiding matrix effects, and developing faster, simpler, more environment-friendly sample-preparation procedures. In this article, we review novel configurations of solid-phase microextraction (SPME), which make the whole process of analysis more selective, more sensitive and more environment friendly. These techniques include hollow-fiber SPME, magnetic dispersive SPME, and ionic liquid-based SPME. Finally, we look ahead to future potential developments of these configurations of SPME.

Contents

1. Introduction

The development of novel sample-preparation techniques with significant advantages over conventional methods, such as reduction in organic-solvent consumption and in sample degradation, elimination of additional sample clean-up and concentration steps before chromatographic analysis, and improvements in extraction efficiency and selectivity, are likely to play an important role in sample pretreatment of analytical chemistry. A successful sample pretreatment method typically has three major objectives:

1 sample matrix simplification;
2 analyte enhancement or concentration; and,
3 sample clean-up [1].

Several new miniaturized extraction procedures, known as liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) techniques, have been introduced and applied with success [2–6].

One of the most popular techniques for preparing samples for analysis to satisfy the requirements of green analytical chemistry is SPME, developed in the 1990s by Pawliszyn and his group [7,8], and implemented by researchers worldwide regarding its fundamental understanding, development of devices and novel applications.

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As a simple, rapid, practical and effective sample-preparation technique, SPME, coupled with various instrumental analytical methods, especially gas chromatography (GC) and high-performance liquid chromatography (HPLC), has been increasingly and widely used to research and to determine trace or ultra-micro levels of inorganic and organic analytes from samples of complex matrices. The enormous popularity of SPME is due to its undoubted merits: simplicity of operation, relatively short extraction time, solvent-free nature, possibility of full automation, and easy coupling with chromatography (such as GC), all of which reduce contamination of the original sample and loss of analytes. SPME can also be used for on-site analysis, and where extraction occurs on-site and only instrumental analysis is performed in laboratory. In addition, using SPME, samples can be collected *in situ*, and reliable results can be obtained for analytes present in trace quantities.

There have been significant advances over the past five years in the development of methods for environmental analysis, and SPME continues to be one of the leading techniques for the extraction of pollutants from aquatic systems [9]. Current trends in the handling of environmental samples include the development of new sorbents for sorptive extractions, the evaluation of new complexing agents, and novel configurations and strategies in SPME.

Food samples are very complex, often containing proteins, fat, salts, acids, bases, and numerous food additives with different chemical properties. A large number of analytical tools, especially chromatography, have been used to analyze the constituents of food in order to control their quality. However, considering the complex constituents in food samples, attention should be focused on those novel pre-treatment methods, extraction techniques with enhanced efficiency and sensitivity, and highly selective sorbents that have been applied in pretreating food matrices. With increasing applications in food samples, SPME plays an important role in food-sample pretreatments.

In this article, we review several configurations of SPME used in food and environmental matrices, which make the whole analysis process more selective, more sensitive and more environment friendly. These techniques include hollow-fiber SPME (HF-SPME), magnetic dispersive SPME (MD-SPME) and ionic liquid-based SPME (IL-SPME). Emphasis is placed on brief descriptions of the unique capabilities and advantages of each modern extraction technique, and how these techniques were exploited to improve absorption and extraction for a variety of analytes. These techniques, based on the partition or adsorption of analytes, were responsible for extracting the majority of the analytes from the sample matrix prior to analysis. Finally, we look ahead to future developments and potential applications of these configurations of SPME methods in food and environmental analysis.

2. SPME techniques in complex matrix

As one of the most widely-used sample-preparation techniques for liquid and gas samples, SPME belongs to the group of sorptive-based extraction techniques, in which the sample is placed in contact with a suitable material, so the availability of different materials to carry out the extraction is essential. SPME combines sampling, extraction, separation and concentration in one step.

In SPME sampling, the analyte is distributed among two or three phases – the fiber coating (or the sorbent materials), condensed samples (liquid or solid sample), and headspace (HS). The kinetics of mass transport of the analytes within the various media determines the SPME sampling time. A distribution constant establishes the equilibrium-concentration ratios of the analyte across each pair of phases. This distribution constant is temperature-dependent, and is also affected by certain factors (e.g., the nature of sorbents, ionic strength, pH of samples, and organic-solvent content). Heating tends to drive analytes out of the liquid phase, but also alters the partitioning of the analytes between the sample and the sorbent. Extraction time and temperature are interrelated variables, and their effect on SPME should not be examined by simply changing one variable at a time [10].

Advances in SPME, *in vivo* and *in vitro*, for the analysis of organic and inorganic compounds from different food and environmental samples, such as beverages, tea, milk, fish, cereals, vegetables, fruits, herbs and medicinal plants, and water samples, which are summarized and discussed below, clearly demonstrate the potential of SPME as a powerful sample-preparation tool in analysis of complex samples. Focus was primarily on the different static configurations of SPME techniques. Research on sample-preparation techniques often therefore focuses on developing new materials to achieve higher selectivity and capacity of the configurations.

2.1. HF-SPME

Polypropylene hollow fibers (PP-HFs) were first introduced by Jeannot and Cantwell in 1996 [11] and He and Lee in 1997 [2] in the form of two- and three-liquid-phase microextraction [12]. Due to its low cost, low carry-over effect, low organic-solvent consumption, and better sample enrichment and clean-up function, PP-HFs were usually used in HF liquid-phase microextraction (HF-LPME) for the protection of microdroplets of extraction solvents, and proved to be practical for the treatment of samples in various areas of study [13,14]. Although high enrichment, clean-up and low solvent consumption are the major advantages of HF-LPME, relatively long extraction times and low selectivity are perhaps its major disadvantages [12,15].

Since the fused-silica or steel fibers for SPME were still comparatively expensive or the polymer coating was fragile [16], PP-HF seems to be a good alternative for SPME due to its cheapness, toughness and repeatable use. However, there is low selectivity and limited specific surface areas in PP-HF [17], and pure PP-HF did not possess much absorption capacity. PP needs to be immobilized or bonded with other absorptive materials to improve its extraction ability, so, with PP-HF as template, zirconia HF in the macro range was successfully synthesized for the first time via a template method using a sol-gel process [18]. The preparation procedure included repeated impregnation of the template in a proper zirconia sol precursor, and calcination to burn off the template, then zirconia HF was produced. The resulting HF is almost identical to its template in terms of morphology, exhibiting a hollow lumen structure. HF-SPME is a new configuration in terms of an entity. It can avoid tedious procedures associated with the powder as the adsorption phase, such as centrifugation or filtration, or adhesion onto the support materials. Zirconia HF can also be used as a substrate, even in an extreme pH and temperature environment. The work has opened the possibility of fabricating numerous interesting inorganic HF structures with a homogeneous controllable wall and porous substructure.

Inspired by Lee's work, a series of oxide HFs {e.g., TiO_2 [17,19], SiO_2 [20], Al_2O_3 [21] and MgO [22]} were fabricated by the sol-gel method and their applications explored in the analysis of natural products [20], food [19,23], environmental [17] and biological [24] samples. Oxide HF even allows direct derivatization on it and could be coupled to ultrasound- or microwave-assisted extraction, and the desorption solution analyzed by GC or HPLC in combination with mass spectrometry (MS). However, inorganic metal oxides still have some common problems, such as relatively low selectivity for analytes in complicated matrices. Thus, further modification, via chemical bonding or coating, to increase the selectivity could be an efficient, easy way to expand its potential applicability.

With the development and innovation of functional materials, there have been an increasing number of applications of carbon nanotubes (CNTs). CNTs exhibit extraordinary structural,