The development of solid-phase microextraction fibers with metal wires as supporting substrates

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This article gives a brief overview of the most relevant examples of solid-phase microextraction (SPME) fibers with metal wires as substrates, mainly concerning different preparation strategies including physical coating, chemical bonding and some other preparation techniques, which involved various sorbent materials (e.g., polymers, nanomaterials, mesoporous materials, metal-organic frameworks, and ionic liquids).

Keywords: Chemical bonding; Conducting polymer; Electrochemistry; Electropolymerization; Magnetron-sputtering technique; Metal wire; Physical coating; Sol gel; Solid-phase microextraction (SPME); Sorbent material

Abbreviations: ATRP, Atom transfer radical polymerization; BTEX, Benzene, toluene, ethylbenzene and xylenes; DDT, Dichlorodiphenyltrichloroethane; EPD, Electrophoretic deposition; GC, Gas chromatography; HPLC, High-performance liquid chromatography; MIP, Molecularly-imprinted polymer; MOF, Metal-organic framework; MS, Mass spectrometry; OCP, Organochlorine pesticide; OPP, Organophosphorus pesticide; PA, Polyacrylate; PAH, Polycyclic aromatic hydrocarbon; PANI, Polyaniline; PDMS, Polydimethylsiloxane; PDMS/DVB, Polydimethylsiloxane/divinylbenzene; PEG, Poly(ethylene glycol); PVC, Polyvinyl chloride; PPY, Polypyrrole; SAM, Self-assembled monolayer; SPME, Solid-phase microextraction; VOC, Volatile organic compound

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1. Introduction

Solid-phase microextraction (SPME) is an efficient, solvent-free, sample-preparation method, which integrates sampling, isolation and concentration into one step. It was first introduced in 1990 by Arthur and Pawliszyn [1] and got automation and optimization by the same group in 1992 [2]. Afterwards, the theoretical principles of both direct-immersion and headspace SPME at equilibrium [3] and non-equilibrium [4,5] were explained mathematically in detail. Based on the clear understanding of theoretical principles and the convenient manipulation of on-line coupling to gas chromatography (GC), high-performance liquid chromatography (HPLC) and mass spectrometry (MS), SPME has been considered as one of the most attractive methods for sample preparation of analytes {e.g., environmental sciences [6], food analysis [7], bioanalysis [8], drug monitoring [9] and toxicology [10]}.

Although the application of SPME is widespread and popular, commercialized fibers still have some important shortcomings (e.g., breakage of the fiber, stripping of the coating, relatively low operating temperature, and instability and swelling in organic solvents) [11]. Numerous efforts have been made to produce novel SPME fibers with improved durability and satisfactory extraction capacity.

The SPME fiber comprises a supporting substrate and a thin layer of sorbent material. Fused-silica fiber has been successfully used as supporting substrate since the first introduction of SPME technology [1]. After removing the protective polyimide layer, the fused-silica fiber can be hydroxylated by alkaline solution and then functionalized (e.g., $-NH_2$, $-SH$ and $-CH{=}CH_2$ groups) by silanization. Different kinds of sorbent material can be coated onto the surface of the silica substrate with different coating techniques based on these multiple functionalizations.

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However, the fused-silica fiber has a fatal drawback. It is very fragile, so it must be handled with great care, and it has limited service lifetime. The recent development of novel SPME fibers has partly been attracted to flexible metal-wire supporting substrates, including stainless steel [12–15], aluminum [16–18], zinc [19], copper [20,21], gold [22,23], platinum [24–27], silver [28–30], and titanium [31]. These metal wires were of strong physical strength, and can be handled with great convenience. Due to the quite different physicochemical properties of these metal wires from fused-silica fiber, there has been a great variety of preparation methods of the metal-wire supported SPME fibers.

In this review, we focus on recent development of SPME fibers with metal wires as supporting substrate, mainly related to different preparation methods and coating materials. Some science and typical strategies published in recent years are simply illustrated and introduced. Finally, we outlined future perspectives and possible challenges in this field.

2. Metal-wire-supported SPME fibers developed by physical coating

Unlike the chemically functional fused-silica fiber, the surfaces of metal wires are usually inert and lack reactive groups. The first metal-wire-supported SPME fiber was prepared through affixing porous alkyl-modified silica particles onto the surface of stainless-steel wire with high-temperature epoxy [12]. The reported lifetime of the fiber was increased over 400 times. But the desorption temperature was limited to 250°C because of the thermal instability of the epoxy adhesive. Farajzadeh and Matin [29] coated the charcoal-polyvinyl chloride (PVC)-tetrahydrofuran viscose suspension onto a silver wire. The proposed fiber showed extremely high extraction capacity, which made 20–30% of the analytes transfer during the first extraction, and that was very peculiar compared with most SPME procedures, which only captured a negligible amount of the analytes in one extraction. Limits of detection (LODs) of the proposed method for alkanes in gaseous and soil sample were 0.05–0.2 μg/mL and 4–16 μg/g, respectively. The same group also prepared an alumina-coated SPME fiber with similar synthesis procedures to analyze polar alcohols in aqueous samples [30]. The stable temperature for desorption was increased up to 300°C in this report.

Because of the wide material compatibility of the physical adhesion process, various candidate sorbent materials were coated onto metal wires by glue and used for different analytical needs (as shown in Table 1).

Du et al. [32] employed C_{16}-MCM-41 as sorbent for SPME. The C_{16}-MCM-41 particles were immobilized onto the stainless-steel wire with epoxy glue. They found that the extraction selectivity could be obtained by polar and dimensional modifications of pores of mesoporous coatings.

A phenyl-functionalized MCM-41-coated fiber [13] was reported by the same group. Distribution ratios of SPME with and without modification by phenyl were 1577/400 for biphenyl, 834/288 for anthracene, 1071/644 for toluene and 867/480 for *p*-xylene. They mentioned that the chemical bonding of phenyl phase on the mesoporous surface improved the selectivity by increasing hydrophobicity at the surface and decreasing pore size of mesoporous coating.

The use of ethyl-functionalized SBA-15 [20], phenyl-functionalized SBA-15 [33] and CMK-3 nanoporous carbon [34] were reported from different laboratories, and showed high stability and selectivity for the extraction of the target analytes.

Also, carbon nanomaterials, including carbon nanotubes (CNTs) [35], graphene [36], and carbon nanocone or nanodisks [37] were physically coated onto metal wires and used for the analysis of organic pesticides and benzenes (BTEX) due to the high extraction capacity of these materials. Analytical parameters (desorption condition, fiber lifetime, LODs for corresponding analytes) of fibers with different sorbent materials prepared by the physical-coating process are included in Table 1. Most desorption temperatures of these fibers were in the range 110–280°C. Increases in lifetimes at corresponding desorption conditions were 40–200 times.

Pawliszyn and co-workers developed some technical innovations of SPME using stainless-steel-supported fibers prepared by the physical-coating process. They introduced a space-resolved SPME technique using a miniaturized segmented C_{18}-silica-particle-coated fiber [44]. The segmented design of the fibers and stepwise successive desorption procedures exhibited high spatial and temporal resolution and increased the capability for high-throughput parallel sampling with a single probe.

They also proposed the first use of SPME in combination with LC-MS for untargeted metabolomic profiling of biological fluids [45]. To obtain the most suitable SPME coatings for both hydrophilic and hydrophobic metabolites, they prepared 42 different SPME fibers and used them to extract 36 metabolites with different physicochemical properties. The proposed SPME methodology reduced ionization suppression, provided free concentration information for hydrophobic analytes and improved metabolite coverage over existing methodologies.

A high-throughput 96-blade SPME system coupled with LC-MS/MS was also developed by the same group for the analysis of complex samples [46]. The biocompatible C_{18}-polyacrylonitrile was coated onto stainless-steel blades by the spraying method. The thin-film geometry of blades brought significant improvement in extraction recoveries and provided low levels of LODs and LOQs. The automated 96-blade system allowed