



Review

Are metal-organic frameworks able to provide a new generation of solid-phase microextraction coatings? – A review



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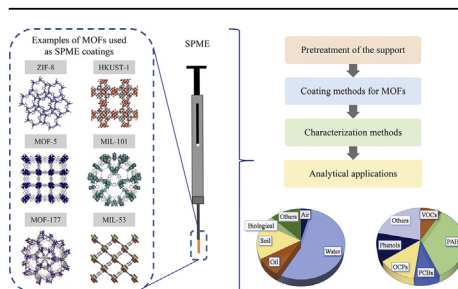
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HIGHLIGHTS

- The utilization of MOFs as novel sorbents coatings for SPME is reviewed.
- Importance of supports pretreatment for accurate preparation of coatings is highlighted.
- MOFs coatings procedures are thoroughly described.
- Analytical applications are deeply described and critically commented.

GRAPHICAL ABSTRACT



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ABSTRACT

Solid-phase microextraction (SPME) is a powerful technique commonly used in sample preparation for extraction/preconcentration of analytes from a wide variety of samples. Among the trends in improving SPME applications, current investigations are focused on the development of novel coatings able to improve the extraction efficiency, sensitivity, and thermal and mechanical stability, within other properties, of current commercial SPME fibers. Metal-organic frameworks (MOFs) merit to be highlighted as promising sorbent materials in SPME schemes. MOFs are porous hybrid materials composed by metal ions and organic linkers, presenting the highest surface areas known, with ease synthesis and high tuneability, together with adequate chemical and thermal stability. For MOF based-SPME fibers, it results important to pretreat adequately the SPME supports to ensure the correct formation of the MOF onto the fiber or the attachment MOF-support. This, in turn, will increase the final stability of the fiber while generating uniform coatings. This review provides a critical overview of the current state of the use of MOFs as SPME coatings, not only highlighting the advantages of these materials *versus* commercial SPME coatings in terms of stability, selectivity, and sensitivity; but also insightfully describing the current methods to obtain reproducible MOF-based SPME coatings.

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1. Introduction

1.1. Overview on solid-phase microextraction: exploring new coating materials

Solid-phase microextraction (SPME) is an extraction and pre-concentration technique developed by Pawliszyn in 1989 [1]. This non-exhaustive extraction approach utilizes a fiber (~1 cm long), made of fused silica or metal core, coated with a sorbent material with film thicknesses between 7 and 100 μm . SPME is based on the partition of the analytes between the sample and the sorbent material. The fiber can be exposed to the sample by direct immersion (DI-SPME), protected with a hollow-fiber (HF-SPME), or in the headspace above the sample (HS-SPME), during a certain period of time (extraction time). SPME can be used under non-equilibration conditions as long as the extraction time is adequately controlled, thus benefiting the establishment of fast extraction methods [2]. Once extracted and preconcentrated in the small amount of sorbent material, analytes will experience desorption in the further analytical technique. Thus, desorption can be thermal: analytes suffer volatilization in the hot injection port of a gas chromatograph (GC), whereas the sorbent material is able to keep its integrity ensuring in this way reutilization. Desorption can be also accomplished by exposing the SPME sorbent material to small amounts of an organic solvent: analytes solubilize in the solvent, whereas the sorbent material of the fiber maintains its integrity. Afterwards, injection of the solvent in a liquid chromatograph (LC) or in capillary electrophoresis (CE) can be performed.

SPME offers many advantages over conventional extraction techniques such as simplicity, easiness of automation, high enrichment factors, low sample volume requirements, and easy reutilization (at least for a certain number of extractions), among others [3]. It is a solvent-free technique when combined with GC, and it only requires small amounts of organic solvents (in the order of microliters of desorption solvent) in LC and CE applications. In this sense, it is clearly an environmental-friendly technique.

Furthermore, SPME can be used in the analysis of gas, liquid (in DI- or HS-), and solid samples (in HS-, or in DI- if samples are properly solubilized and/or extracted prior to SPME); and for the determination of volatile, semi-volatile, and non-volatile analytes, thus demonstrating great versatility [4]. Apart from the unquestionable interest and applicability of SPME in targeted and non-targeted analyses in a variety of fields [5–7], several strategies involving SPME have also been devoted to: (i) theoretical studies using the negligible depletion method [8,9], (ii) improving the extraction performance using vacuum-assisted HS-SPME [10], (iii) in-tube SPME applications [11]; (iv) internally cooled fiber designs [12], and (v) *in vivo* studies [13], among others.

As disadvantages, SPME fibers can exhibit certain fragility, and carry-over effects can be quite important when SPME is combined

with LC and CE [2]. It is also important to mention the limited number of commercially available sorbent coatings. There are only seven materials commercially available for SPME from Supelco: carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polyacrylate (PA), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), carbowax/divinylbenzene (CW/DVB), and carbowax/templated resin (CW/TPR).

To overcome these limitations, recent advances in SPME are focused on the development and evaluation of novel materials as sorbent coatings, able to provide high extraction efficiency as well as high selectivity while maintaining high mechanical and chemical stability [14]. It is undoubted that the linkage of materials science with analytical chemistry, particularly regarding sample preparation, is being quite fruitful [15]. Thus, ionic liquids (ILs), polymeric ionic liquids (PILs), graphene, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), other nanomaterials, and molecularly imprinted polymers (MIPs), merit citation among novel materials in SPME.

ILs and PILs have been successfully employed to design new SPME coatings [16] due to their ease of synthesis and high tunability, permitting the preparation of highly selective fibers. In the case of ILs, some pretreatments of the solid support of the fiber are required to obtain reusable and more stable coatings [17]. In this sense, PILs have had more success as SPME materials than neat ILs [16]. The solid nature of the PILs together with their high thermal stability have made them adequate substitutes for commercial coatings, especially for GC applications [18–20]. Recently, the high stability of these materials towards organic solvents and low pH values have been demonstrated when used in LC applications [21,22].

Graphene, SWCNTs, and MWCNTs, have also been widely employed as novel SPME sorbent coatings, either neat [23,24] or in combination with other materials thus generating more efficient composites [25,26]. These materials present high thermal, chemical, and mechanical stability, and great affinity towards organic compounds. Besides, their unique structures and high surface areas allow rapid extraction and desorption of the compounds.

With regards to the use of other nanomaterials as SPME sorbents, nanoporous silica [27], nanostructured conducting polymers [28], and a variety of metals and metal oxides [29], have been explored, mainly for the extraction of hydrophobic compounds. Their use in SPME is clearly favored by their high stability and ease of synthesis [30].

MIPs have also been employed as sorbent coatings for the analysis of a wide variety of complex samples [31]. These highly crosslinked polymers are characterized by the presence of molecular recognition sites for specific compounds in their structure, which make them highly selective materials. They are cheap, easy to prepare, and exhibit high chemical and mechanical stability [32]. However, the complete removal of the template used during their

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