



Recent developments and applications of different sorbents for SPE and SPME from biological samples



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ARTICLE INFO

Keywords:

Solid phase extraction
Solid phase microextraction
Biological samples
Pre-concentration

ABSTRACT

Solid phase extraction (SPE) and solid phase microextraction (SPME) are among the most significant sample clean-up and pretreatment techniques, which have attracted a considerable interest in the pre-concentration and determination of a wide variety of analytes in biological, pharmaceutical, environmental, industrial and food samples. The purpose of this review article is to focus on the latest advancements and applications of SPE and SPME methods based on new nanomaterial adsorbents for separation, concentration and determination of different analytes in biological media. To this end, some sorbents such as metal organic frameworks, molecularly/ion-imprinted polymers, carbon nanotubes, magnetic nanoparticles, graphene and graphene oxide, and metallic nanoparticles are discussed here.

1. Introduction

The concentration of both organics and inorganics in complicated matrices such as biological samples is lower than the limit of detections of many analytical instruments; therefore, sample pretreatment should be considered as a crucial part of any analytical procedures prior to analysis. This process provides clean-up, analyte pre-concentration, sensitivity, and signal enhancement as well. Among different sample preparation techniques, solid phase extraction (SPE) and solid phase microextraction (SPME) are the most frequently applied approaches for trace enrichment of a wide variety of analytes in diverse matrices involving biological, industrial, environmental, and food samples [1,2].

The concept of SPE is on the basis of analytes partitioning between the liquid phase and the solid sorbent. This technique provides the enrichment of analytes from solution by adsorption of the target compounds on a solid sorbent. As a consequence, an appropriate choice of sorbent is essential to improve the selectivity, sorption capacity, and efficiency of the SPE procedure. It is worth mentioning that the selection of sorbent relies not only on the identity of the analyte and its interaction with the sorbent but also on the nature of sample matrix. In addition, SPE enables the recovery of analytes in a small volume of an appropriate eluting solution to provide a desirable pre-concentration factor necessary for target analysis.

In the past, the most common classic sorbents employed in SPE procedure mainly included the chemically bonded silica with different functional groups, polymer-based sorbents, and carbon-based materials.

However, due to some restrictions such as limited physical and chemical stability in low or high pHs, low capacity, and limited reusability associated with these conventional sorbents, in recent years, an important endeavor has been dedicated to the introduction of new solid sorbents for SPE to facilitate the extraction procedure in complicated matrices [3–5].

Meanwhile, SPME is well-established as one of the most popular green approaches for pretreatment and enrichment of a broad spectrum of analytes from complicated samples. In SPME, an attenuate covering of the extraction phase is plastered over the fibers at which the target compounds can be extracted from sample solutions. In direct immersion form of SPME (DI-SPME), the analytes are extracted directly from sample media, while in headspace configuration (HS-SPME) the SPME coating is placed in the headspace of the investigated sampling environment. Simplicity, sensitivity, being environmentally friendly, and rapidity are the most remarkable merits associated with this sampling technique [6]. The nature of fiber coating materials is an essential factor affecting the efficiency of the SPME procedure; therefore, in recent years, a great deal of research has been performed to establish novel coating materials in order to enhance the efficiency of the enrichment process in SPME.

Biological samples (e.g., hair, blood, plasma, and urine) are considered as a complicated matrix because they contain extra organic and inorganic compounds such as proteins, salts, and acid-base substances along with the presence of ultra-trace amount of the analyte of interest [7]. As a result, due to either the low concentration level of analytes or

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presence of impurities and interferences, it is essential to extract and enrich the target compounds from these complicated samples preceding to instrumental detection. In this respect, SPE and SPME have become two preferable pretreatment techniques for subsequent extraction and determination of various analytes from several biological media.

The outline of this review is to provide a comprehensive information about the development and applications of new solid materials such as molecularly/ion-imprinted polymers (MIPs/IIPs), magnetic nanoparticles (MNPs), metal organic frameworks (MOFs), graphene and graphene oxide (G and GO), and metallic nanoparticles as sorbents or fiber coatings in SPE and SPME of diverse analytes in biological samples [8–15].

2. Molecularly/ion-imprinted polymers (MIPs/IIPs)

Molecularly-imprinted polymers (MIPs) are a class of synthetic sorbents appeal to many chemists, biologists, and environmentalists, due to such inherent merits as chemical/mechanical stability, thermal strength, high selectivity to target analyte, and good reusability. In recent years, MIPs have found widespread applications as selective and efficient sorbents or fiber coating materials in biological, food, and environmental matrices [16]. Normally, a three-dimensional structure of MIP is produced by the reaction of the target compound (template) and a proper monomer in the presence of a cross-linking agent to provide cavities for selective recognition of the imprinted molecule, after polymerization process. The formation of specific binding sites between the polymer and the template can be attributed to the self-assembly of the template and the functional monomer. The subsequent release of the imprint analyte from the synthesized polymer network allows the selective rebinding of the template in the sample solution [16]. In this section, several examples of molecularly-imprinted solid phase extraction (MISPE) for the enrichment of different target molecules in biological samples will be described.

In 2013, Ebrahimzadeh et al. [17] reported the application of MISPE for the extraction and determination of haloperidol from plasma and urine samples. In their study, the haloperidol imprinted polymer was prepared by precipitation polymerization using methacrylic acid (MAA) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross linker, and 2,2'-azobisisobutyronitrile (AIBN) as an initiator. Then the template was removed from the MIP network via solvent extraction using a methanol-acetic acid-trifluoroacetic acid mixture (79.9:20:0.1), and the resulted polymeric powder was used for subsequent SPE procedure, followed by HPLC analysis. Similarly, a surface molecularly-imprinted polymer (SMIP) was prepared for the selective adsorption of ampicillin sodium from blood samples [18]. In this approach, the ampicillin-MIP was prepared via surface imprinting process, in which an MIP shell was anchored at the spherical surface of silica gel. Then, the prepared MIP was applied to separation of the target ampicillin contained in blood samples, with a limit of detection of $0.15 \mu\text{g mL}^{-1}$.

In 2016, a molecularly-imprinted solid phase microextraction fiber (MIP-SPME_f) was applied to the selective enrichment of the antiviral drug, abacavir (ABA) [19]. The ABA-MIP-SPME_f was synthesized via radical polymerization of acrylic acid (AA), EGDMA, and AIBN. The prepared SPME fiber was immersed into a sample solution containing ABA for a time period of 40 min. After extraction, the target ABA was eluted from the fiber surface using 1 mL of MeOH/formic acid via ultrasonication. After that, the extracted analyte was injected into the LC-MS system for subsequent analysis. Finally, the SPME procedure was employed for sensitive and reliable analysis of the target drug in urine samples.

The concept of ion-imprinted polymer (IIP) was first presented by Nishide et al. [20] for identification of metal ions. The production of IIPs starts with the reaction between a metal ion and a ligand to form a complex. After polymerization, the imprint ion can be leached from polymer structure using a proper solvent such as a mineral acid [21,22]. On behalf of such advantages as simplicity, low cost, high capacity, and

durability in different chemical environments, the IIPs have revealed prevalent utility in SPE of a diverse range of metal ions at trace levels from intricate samples [23–27]. Moreover, IIPs have been employed preferably for selective separation of different metal ions from other coexisting species, which may lead to subsequent clean-up of the analytes.

Up to now, the merging of MIPs/IIPs with other nanoparticles such as magnetic nanoparticles, carbon nanotubes, and quantum dots have been employed to enhance either the selectivity or the sensitivity of the SPE procedure for enrichment of various compounds. In this case, the prepared polymer-coated nanoparticles exhibited not only a faster mass transfer of analytes into the imprinted cavities but also a higher adsorption capacity [28–31]. Recently, a novel magnetic-IIP was proposed for the selective extraction and pre-concentration of Pb(II) ions from human hair samples followed by determination using graphite furnace atomic absorption spectrometry (GFAAS) [32]. In this work, the Pb-IIPs were synthesized using EGDMA, 4-vinylpyridine (4-VP), 2,3,5,6-tetra(2-pyridyl) pyrazine (TPPZ), and MWCNTs as a cross linker, functional monomer, ligand, and carrier, respectively. Under optimum conditions, the LOD was 2.4 ng L^{-1} with an enhancement factor of 200. The proposed MSPE method offered good linearity, high adsorption capacity, and simplicity.

In general, both MIPs and IIPs offer excellent extraction efficiency as either SPE sorbent or SPME fiber coating for determination of target analytes at trace concentration levels when they are exposed to various biological matrices such as urine, serum, and blood samples. Table 1 summarizes the latest applications of MIPs and IIPs for the enrichment of a variety of target organic and inorganic compounds from different biological samples.

3. Carbon nanotubes (CNTs)

CNTs in the form of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are made up single or several layers of graphene sheets [33]. SWCNTs diameters can attain 3 nm, while in case of MWCNTs the diameter can reach to 100 nm [34]. Based on the graphene layers arrangements, CNTs exhibit either conductive or semi conductive properties. This group of nanomaterials reveals remarkable properties, namely, large surface area together with desirable thermal, mechanical, and chemical stabilities. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface reveal strong interactions with other molecules and make them a proper sorbent for enrichment process. In addition, the surfaces of CNTs are capable of being functionalized to enhance their selectivity and dispersibility in different solvents [34]. For instance, Barbosa et al. [35] modified an oxidized CNTs with a layer of bovine serum albumin (BSA) to extract lead(II) ions from untreated human serum samples. For this purpose, the BSA molecules were fixed at the surface of CNTs using glutaraldehyde as a cross linker agent. The resulted material, named as restricted-access CNTs (RACNTs), was successfully used in an on-line solid phase extraction system for enrichment of Pb^{2+} ions. Low limit of quantification, good precision, accuracy, and reusability were the main advantages associated with this method. Moreover, in recent applications, it has been shown that the magnetic properties can be merged into the CNTs to provide higher adsorption capacity, better dispersity in water, and more convenient separation of the solid sorbent. For this purpose, Bigdelifam et al. [36] extracted fluoxetine from urine samples using charge transfer complex formation after solid phase extraction by $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ nanocomposites. The use of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ as a sorbent facilitated the extraction procedure and pre-concentration of the fluoxetine from sample solution without using centrifugation or filtration.

The application of CNTs as fiber coating material provides a large surface area with fast mass transfer characteristics for the enrichment of target molecules from complicated biological samples. The interaction sites available either on the walls or in internal spaces between the

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