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Review

Applications of Nanomaterial Coatings in Solid-Phase Microextraction (SPME)

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Abstract: This review explores the advances in developing adsorbent materials for solid-phase microextraction (SPME), focusing on nanoparticles, nanocomposites, and nanoporous structures. Nanoparticles, including those of metals (e.g., gold, silver), metal oxides (e.g., TiO_2, ZnO), and carbon-based materials (e.g., carbon nanotubes, graphene), offer enhanced surface area, improved extraction efficiency, and increased selectivity compared to traditional coatings. Nanocomposites, such as those combining metal oxides with polymers or carbon-based materials, exhibit synergistic properties, further improving extraction performance. Nanoporous materials, including metal–organic frameworks (MOFs) and ordered mesoporous carbons, provide high surface area and tunable pore structures, enabling selective adsorption of analytes. These advanced materials have been successfully applied to various analytes, including volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), pesticides, and heavy metals, demonstrating improved sensitivity, selectivity, and reproducibility compared to conventional SPME fibers. The incorporation of nanomaterials has significantly expanded the scope and applicability of SPME, enabling the analysis of trace-level analytes in complex matrices. This review highlights the significant potential of nanomaterials in revolutionizing SPME technology, offering new possibilities for sensitive and selective analysis in environmental monitoring, food safety, and other critical applications.

Keywords: nanomaterials; solid-phase microextraction (SPME); porous materials; nanoporous carbons; gas chromatography coupled SPME; SPME fiber coatings; selective adsorption; environmental monitoring; trace analysis

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1. Introduction

Microextraction is a sampling technique characterized by the use of a significantly smaller volume of extractant (liquid or solid) relative to the sample volume. Consequently, only a portion of the analyte is extracted, resulting in a non-exhaustive process. SPME is a specific microextraction method that relies on analyte partitioning between a sample matrix and a stationary phase immobilized on a fiber. This equilibrium-based process is governed by Nernst's partition coefficient, with higher values indicating greater analyte extraction efficiency. The selection of the fiber coating is crucial, as it determines the selectivity and capacity for different analytes [1,2].

Invented in the late 1980s, SPME revolutionized sample preparation by offering a solvent-free, single-step approach. SPME eliminates the need for bulky extraction processes, allowing for rapid analysis both in the lab and at the sampling site. This innovative technique utilizes a tiny fiber coated with a specific material to directly extract and concentrate

analytes from the sample. This translates to faster processing times, reduced waste disposal costs, and potentially improved detection limits [3–5].

SPME is a solventless sample preparation method that relies on achieving equilibrium between the sample and a coated fiber, and involves these steps:

1. Extraction: A fused silica fiber with a specific coating (polymer or sorbent) is exposed to the sample matrix. Target analytes partition from the sample into the coating based on their affinities for each. This selectively concentrates the analytes on the fiber. Extraction can be achieved through direct immersion (DI) or headspace (HS) sampling [6].
2. Desorption: The fiber, loaded with concentrated analytes, is then transferred to an instrument like a gas chromatograph (GC) or high-performance liquid chromatograph (HPLC). Inside the instrument's injector, the analytes are desorbed from the coating and introduced into the analytical system for separation and quantification [7]. Desorption is primarily accomplished by exposing fibers to high temperatures in the GC injector, although solvent immersion can also be used [6].

With two opposing effects, the extraction temperature in SPME has a complicated role. On the one hand, analytes' diffusion coefficient increases with increasing temperature, encouraging their migration towards the extraction phase. In contrast, high temperatures decrease the analytes' distribution constant, which lessens their retention on the fiber because adsorption is an exothermic process. Pawliszyn developed a unique mechanism that cools the fiber and heats the sample at the same time in order to address this difficulty. This dual-action configuration optimizes both the diffusion and adsorption processes, increasing the mass transfer of analytes from the sample to the fiber coating and increasing extraction efficiency [8].

The type of coating applied to the SPME fiber is critical to its extraction and desorption effectiveness because it influences the distribution coefficient of analytes between the stationary and bulk phases. It serves to distinguish analytes from other substances. Various coatings have been created to improve the extraction of a wide spectrum of analytes. For SPME procedures to be effective under different conditions, a robust sorbent must be properly selected. Surface active groups, molecule size, and polarity all affect the selectivity of coating materials [9,10].

In the traditional in-fiber mode of SPME, a sorptive phase immobilized on an inert support is used to extract analytes directly from the sample or its headspace. Polymeric coatings' exceptional chemical and thermal durability makes them popular sorptive phases. For a wide variety of target analytes, their polarity can be adjusted by mixing various materials, resulting in the best extraction performance. Metal–organic frameworks (MOFs), carbon fiber, graphene, polypropionates, polydimethylsiloxane (PDMS), polyacrylate (PA), Carbowax, polydimethylsiloxane–divinylbenzene (PDMS–DVB), and carboxen–polydimethylsiloxane (CAR-PDMS) are examples of common coatings. Despite their widespread use, polymer coatings have significant drawbacks, including low heat resistance, swelling when organic solvents are present, and limited extraction efficiency. To tackle these problems, scientists have looked into nanomaterials, which have benefits like a large surface area, mechanical strength, and special chemical and physical characteristics. Materials including nanofibers, nanoparticles, and nanotubes have greatly improved SPME fiber extraction efficiency and capacity. They successfully surpass the restrictions placed by the small diameter of conventional fibers thanks to their large surface area and large number of active adsorption sites. The continuous creation of new coatings, such as molecularly imprinted polymers, polymeric ionic liquids, and other nanomaterials, is still a key area of SPME research. By strengthening the technique's selectivity, sensitivity, and adaptability, these developments hope to make it possible to use it in more challenging analytical situations [10–15].

Nanotechnology enables the design of materials with exceptional properties [16]. Nanomaterials with remarkable chemical and physical attributes are gaining significant attention in the field of separation science. Nanomaterials are now being used in extraction procedures because they have tiny pores and high surface areas that make them more efficient at extracting substances. These materials are also used as SPME coatings because they can withstand high temperatures. Future reviews on SPME coatings and nanomaterials in analytical sample preparation should focus on the use of nanomaterials for SPME coatings [17,18].

In order to obtain the necessary results, an analytical procedure usually consists of several steps, such as sample preparation (including sampling), chromatographic methods (LC or GC), capillary electrophoresis, detection, and data processing. SPME has become a useful technique for sample preparation because of its ease of use, effectiveness, and capacity to combine extraction and preconcentration in a single step. The enhancement of SPME and other sample preparation methods is greatly aided by nanoparticles. Their physical characteristics and chemical characteristics, like sorption capacities, are frequently advantageous. In order to simplify procedures and make it possible to analyze very small sample volumes, nanoparticles—or chemically modified variants—are utilized for sample cleanup and analyte preconcentration. This development is especially helpful for performing studies with small sample amounts or for investigating novel sample matrices where the sample amount is minimal [19].

The objective of this review is to evaluate the performance of various nanomaterials used in SPME fibers, with a particular emphasis on sensitivity, selectivity, durability, and suitability for detecting specific analytes. The assessment seeks to determine which materials and production techniques have exhibited the best overall performance across a variety of applications.

In this review, we focus on the different applications of nanomaterials as coatings on SPME fibers. We also review the different types of nanomaterials that could be used as coatings, for example, metal oxide nanoparticles, carbon nanoparticles, metal nanoparticles, and others. We conclude the review by looking at the performances of the different types of nanomaterials as SPME coatings.

2. The SPME Device

2.1. The SPME Design

The SPME device resembles a syringe with a small, cylindrical fused silica fiber attached to stainless steel tubing for added durability, as seen in Figure 1. The fiber is traditionally coated with a thin layer of various polymeric stationary phases, enabling it to effectively adsorb analytes from different sample matrices. The coated fiber is inserted into a needle, which is part of the syringe-like structure [20–22]. The SPME device can be replaced and reused. The fiber is easier to put into samples or headspace for analyte extraction because of its compact form and cylindrical structure. Furthermore, without requiring adjustments to the equipment, it may be easily positioned in the interface of a high-performance liquid chromatograph (HPLC) or the desorption chamber of a gas chromatograph (GC). For reliable results during adsorption and desorption, precise control over plunger movement and timing is crucial. Analyte loss can be caused by improper handling, especially during field sampling. Analyte escape can be minimized by cooling the needle opening or sealing it with a septum [23].

2.2. Working Operation of the SPME

In SPME, as seen in Figure 2 (working principle), the fiber is initially retracted into the syringe needle and inserted into a sealed vial with a septum cap. The choice of fused silica

fiber depends on the analyte being studied. Prior to analysis, the fiber must be cleaned with solvent to remove any contaminants that could affect the chromatogram. SPME extraction is commonly performed in two ways: (1) headspace SPME (HS-SPME), where the fiber is exposed to the vapor phase above the sample, and (2) direct-immersion SPME (DI-SPME), where the fiber is immersed in liquid. Analytes are typically desorbed from the fiber via thermal desorption in a gas chromatograph, eliminating the need for organic solvents. For liquid chromatography (LC), desorption can be performed using polar organic solvents like methanol or acetonitrile, which allows for increased sensitivity. Depending on how strongly the analytes are adsorbed, desorption can be dynamic (with a moving mobile phase) or static (with the fiber immersed in solvent for a set time).

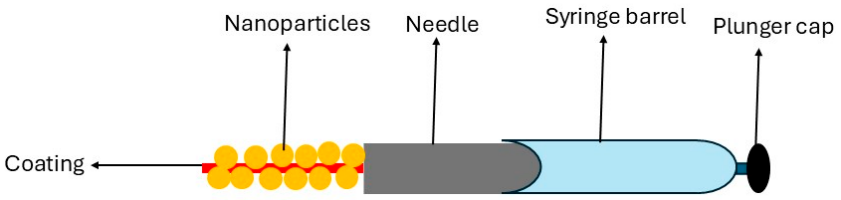


Figure 1. The SPME device.

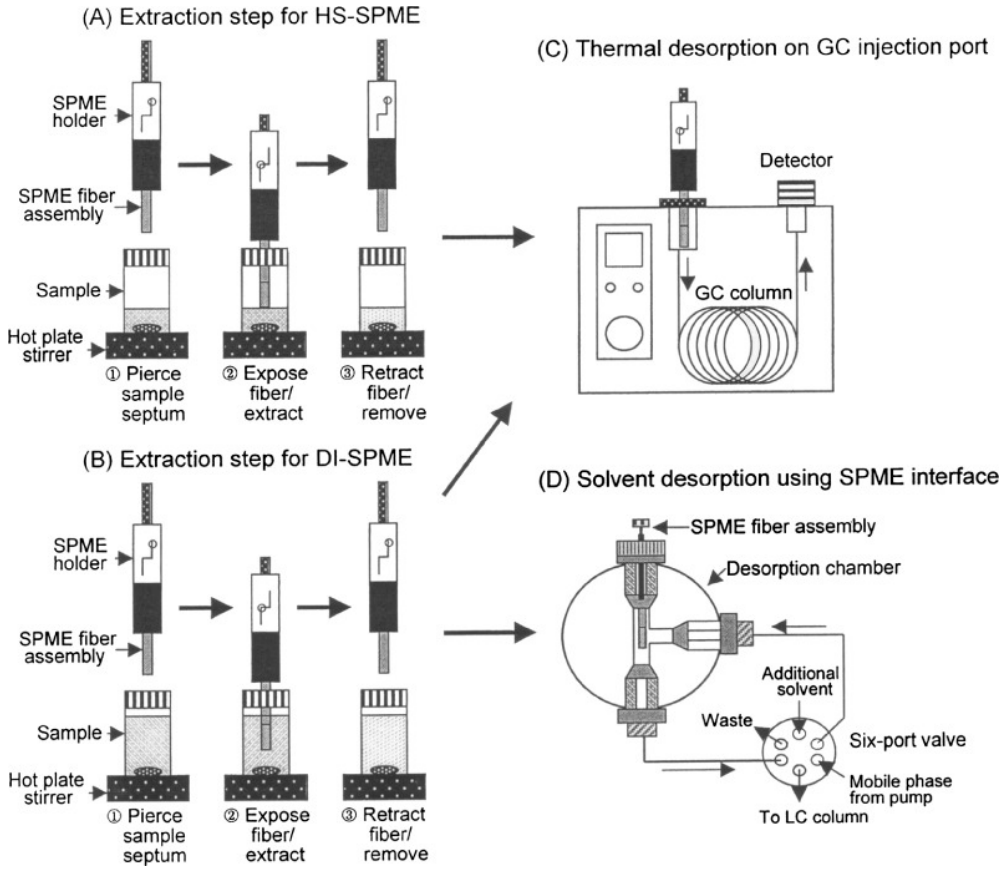


Figure 2. (**A**,**B**) Working principle of SPME using different extraction techniques. (**C**,**D**) Desorption of analytes from SPME fiber injected into the GC injection port. Reprinted with permission from [24]. Copyright 2004, Wiley.

3. Range of Compounds to Which SPME Has Been Applied

SPME has been applied to the analysis of different compounds including volatile organic compounds (VOCs), food components, environmental analytes, flavors, and so on. In this section, we will look at the range of compounds to which SPME analysis has been applied.

3.1. Volatile Organic Compounds (VOCs)

The non-invasive nature of volatile organic compound (VOC) analysis and its comparatively inexpensive sample and analysis costs make it a viable method for identifying putative cancer biomarkers and other applications. Since its introduction by Pawliszyn in 1989, SPME has gained popularity as a method for extracting volatile organic compounds (VOCs) from both in vitro and in vivo samples. Because of its ease of use, lack of solvents, automation potential, and compatibility with both liquid and gas chromatography, SPME is widely used in many different industries [25].

Lim et al.'s study identified twelve compounds that distinguish rice from Korea and China by analyzing white rice from the two nations using DVB/CAR/PDMS-SPME with GC-MS. More research is needed on 10 new hydrocarbon determinants, while hexanal and 1-hexanol levels were related to storage and environmental conditions. They came to the conclusion that additional food products could benefit from this technique, which can differentiate white rice based on its origin [26].

A study by Poli et al. evaluated the potential of aldehydes, which are biomarkers of oxidative stress, as non-small-cell lung cancer (NSCLC) diagnostic tools. Linear aldehydes (C3–C9) in exhaled breath were quantified by the researchers using a solid-phase microextraction (SPME) technology with GC/MS analysis. With detection and quantification limits of 1×10^{-12} M and 3×10^{-12} M, respectively, the approach showed excellent linearity over a range of 3.3–333.3 $\times 10^{-12}$ M. Precision (as a percentage RSD) was between 7.2 and 15.1%, while accuracy was above 93%. At +4 °C, aldehyde stability in a Bio-VOC® tube lasted 10–17 h, but with certain fiber storage, it lasted for more than 10 days. In a clinical study, breath samples from 40 NSCLC patients and 38 asymptomatic non-smokers revealed significantly higher aldehyde levels in the NSCLC group, with age and smoking having no effect. A 90% discrimination power based on aldehyde patterns was verified by multivariate analysis, indicating that these chemicals may improve the sensitivity and specificity of VOC-based diagnostics for non-small-cell lung cancer. The study emphasizes aldehydes' potential as trustworthy biomarkers for the early diagnosis of lung cancer [27].

To identify and measure volatile organic chemicals (VOCs) in human breath as possible lung cancer biomarkers, Rudnicka et al. conducted a study. Using gas chromatography–time-of-flight mass spectrometry (GC–TOF/MS) for analysis and SPME for preconcentration, the method produced quick and sensitive detection at parts-per-billion (ppb) levels. Linearity between 0.83 and 234.05 ppb, detection limits between 0.31 and 0.75 ppb, and precision with relative standard deviations (RSDs) below 10% were all displayed by the accuracy-optimized approach. Using sophisticated statistical techniques, the study found important volatile organic compounds (VOCs) linked to lung cancer, indicating that this non-invasive technique is a promising early screening tool [28].

In order to collect volatile organic compounds (VOCs) from biological materials such as blood, breath, buccal swabs, and urine, Kusano et al. devised and refined a headspace SPME approach employing forensic and clinical kits. Using this method, different samples from the same person might be directly compared. VOCs could be detected with great sensitivity using their optimized SPME-GC/MS approach; urine had the highest detection limits while breath samples had the lowest [29].

3.2. Food

Evaluating nutritional value, guaranteeing freshness, processed products' quality control, and detecting dangerous pollutants and food additives all depend heavily on food analysis [30]. Analysis is difficult since dietary components constitute a complex matrix. Since analytes are frequently present in trace levels, an optimal approach should combine isolation, preconcentration, and precise quantification [23]. With its expanding

applications, SPME is becoming more and more significant in food sample pretreatment. Solid-phase extraction (SPE), Continuous-Steam Distillation Extraction (SDE), headspace (HS), Nitrogen Purge and Trap (NPT), and Supercritical Fluid Extraction (SFE) are some of the conventional extraction techniques over which SPME provides a number of clear advantages [31].

Barboni et al. identified 44 chemicals in a study that used HS-SPME/GC and/or GC/MS to analyze 67 juices from mandarin, clementine, and hybrids. According to their findings, mandarin juice had higher levels of γ-terpinene (21.1%) and lower levels of limonene (66.3%) than clementine juice, which was highest in limonene (90.0%) and lowest in γ-terpinene (1.2%). The limonene/γ-terpinene ratios of hybrid juices varied, but their profiles were similar. According to their findings, 7% of hybrids displayed abnormal profiles because of para-cymene or terpinen-4-ol, 48% resembled clementine, and 45% were more like mandarin [32].

Using cutting-edge methods (HS-SPME and GC-O (gas chromatography–olfactometry)), Mounchili et al. investigated the effects of giving fresh silage to nursing cows prior to milking. They discovered that using butane-2-one and dimethyl sulfide levels as markers may result in milk having an unpleasant flavor. While Mounchili et al. encouraged more research using absolute VOC concentrations, they also stated that these data might support a diagnostic tool as an alternative to sensory testing. They determined that rather than specific molecules, off-flavors are caused by changes in concentrations of common aromatic compounds (AACs), and they recommended more research to measure these AACs and look into the effects of bacteria on milk volatiles [33].

3.3. Environmental Analysis

There is a great deal of research showing detrimental impacts of environmental organic pollutants on both humans and animals, making human exposure to them a serious concern. Understanding the bioaccumulation and toxicity of these contaminants in environmental toxicology and clinical studies requires the monitoring of these pollutants and endogenous metabolites in organisms [34].

SPME is a well-established, green process for extracting and preconcentrating analytes across a wide range of matrices. Since its inception in the early 1990s, SPME has swiftly progressed in terms of coating materials, geometries, and uses. SPME was originally developed for environmental investigations, but it has now become a major method for analyzing volatile and semi-volatile organic compounds (VOCs and SVOCs). SPME's versatility, particularly in its headspace version (HS-SPME), has made it widely used for pollutants with diverse physicochemical features, including medicines, insecticides, and metal–organic compounds. This adaptability addresses issues in traditional sample preparation, indicating a significant impact on future analytical procedures [35,36].

In their work on the procedure for the control of butyl and phenyl tin pollution in the environment by GC-FPD, Aguerre et al. found that $NaBEt_4$ ethylation–SPME extraction–GC-FPD (gas chromatography–flame photometric detection), supplemented with acidic extraction for solid matrices, is a promising method for identifying organotin chemicals in water and complicated environmental samples. They discovered that mechanical stirring greatly enhanced analytical performance during adsorption, with detection limits that are 10–700 times lower than classical liquid–liquid extraction and 2–20 times lower than SPME with magnetic stirring. Their optimized SPME approach produces results comparable to isooctane extraction and detects organotins at concentrations lower than 1 ng/L as Sn in aqueous samples. While co-extracted organic matter in complex matrices can influence triphenyl tin (TPhT) responses, recent research on adsorption–desorption

behavior suggests that this approach is a useful tool for routine organotin detection in water [37].

Table 1 contains information about the different types of compounds that have been detected by SPME, the types of nanoparticles used in SPME fiber coating, and their analytical applications.

Table 1. Classes of compounds analyzed using solid-phase microextraction based on nanomaterial coatings.

Type of Compound	Examples	SPME Coating Materials	Applications	Reference
Volatile Organic Compounds (VOCs)	Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)	Carbon-ZrO_2 Nanocomposites, PDMS, MOFs	Environmental monitoring, water analysis	[38]
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene, Anthracene, Pyrene	Mesoporous Carbon, Carbon Nanotubes (CNTs)	Food safety, environmental analysis	[39]
Pesticides	Organochlorines, Organophosphates	3D graphene–Iron Oxide Nanocomposite (3D-G-Fe_3O_4)	Food and water analysis	[40]
Nicotine and Metabolites	Nicotine, Cotinine, Nornicotine	Nitrogen-rich Porous Polymers	Neuroscience research, pharmacokinetics	[41]

4. Advances in the Adsorbent Type Used in the Extraction Phase of the SPME Fiber

The most common SPME setup consists of a fused silica rod with a thin polymeric coating, but this configuration has several limitations, including low operating temperatures, instability in organic solvents, limited mechanical durability, and difficulty extracting polar compounds from aqueous solutions. These difficulties have prompted ongoing advances in SPME geometries, setups, and extraction phases, with recent efforts focusing on trace analysis and challenging applications. SPME research focuses on the development of new sorbents and fiber coatings to improve selectivity, sorptive capacity, and thermal, chemical, and mechanical stability. This work intends to improve device lifetime and sensitivity by refining the enrichment process and expanding SPME's applicability, particularly in complicated matrices for a variety of analytical applications [42–44]. Figure 3 is a description of the advances in materials chemistry to fabricate different materials for use in SPME [45]. In this section, we further discuss the different types of sorbent materials that can be used to increase extraction efficiency in SPME operations, including nanoparticles, silicon-containing nanostructures, nanocomposites, and others.

4.1. SPME Based on Nanoparticles

Nanoparticles are generally defined as being in the range of about 1–100 nanometers in diameter. Compared to bulk materials, their physical and chemical properties are different because they contain fewer atoms, with a larger percentage at or close to the surface. Definitions of nanoparticle size can differ, but when a property differs sufficiently (by a few percent) from the bulk material, a practical upper limit is attained [46].

Researchers frequently use nanoparticles to clean and recover target analytes from intricate sample matrices. Their large surface area and strong affinity for particular analytes make them excellent sorbents that greatly improve the sensitivity and selectivity of analytical procedures. Furthermore, nanoparticles are prized for their remarkable adsorption characteristics, high preconcentration factors, reusability, and simplicity of surface modifications. These characteristics help improve the sample preparation procedure [47].

Nanoparticles (NPs) are effective as adsorbents in various separation and preconcentration procedures, such as SPE, SPME, and μ-solid-phase extraction (μSPE), making them crucial for environmental pollutant analysis. They are also used in chromatographic procedures such as GC and HPLC in which NP-coated columns act as stationary phases. NPs are preferred for extraction methods due to their large surface area and porosity, which

improves extraction efficiency and greater extraction rates. Their superior mechanical, chemical, and thermal stabilities make them ideal for SPME coatings. Ongoing research focuses on producing cost-effective extractive materials that improve selectivity and capacity while reducing sample and solvent usage. Furthermore, these materials are sought out for adequate stability to allow reproducibility and reuse [48–50]. Recent reviews have focused on several types of nanoparticles and their applications in microextraction; we will also be focusing on the different types of nanoparticles used in SPME subsequently.

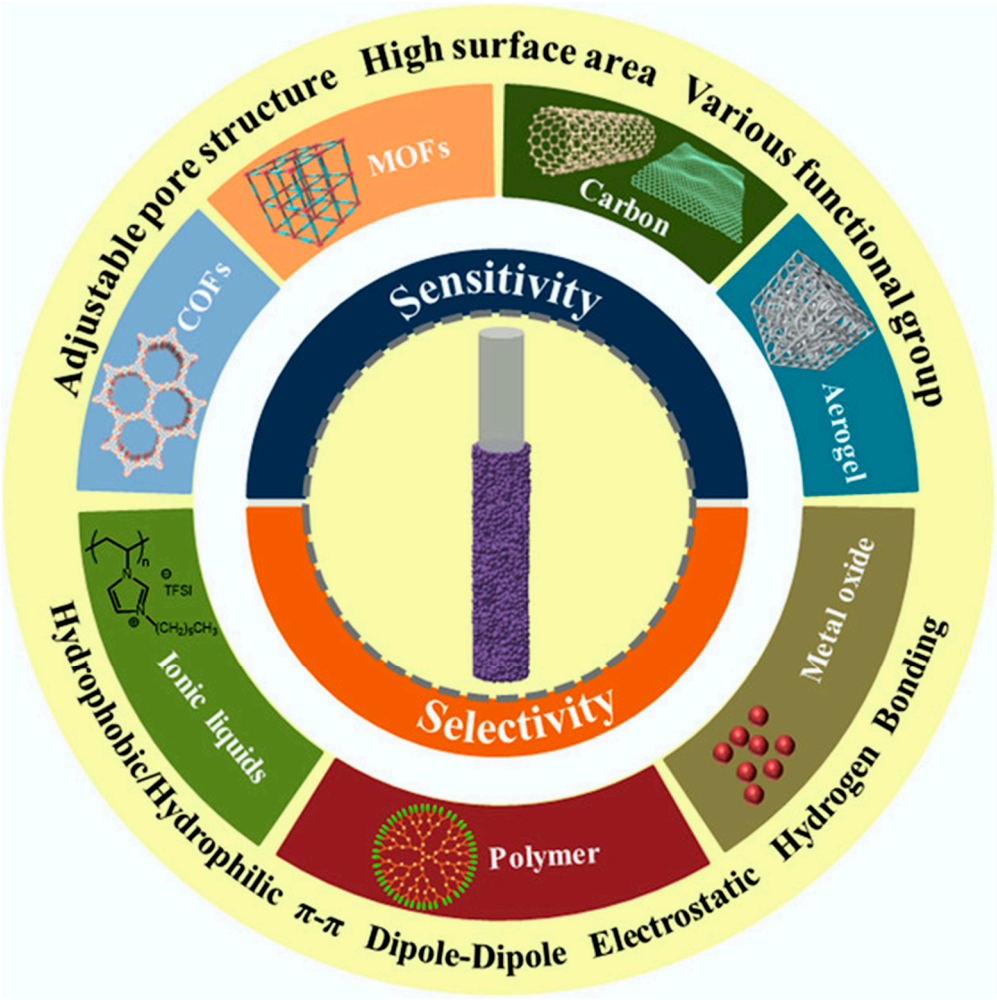


Figure 3. Advances in materials chemistry for the fabrication of different materials for use in SPME fibers. Printed with permission from [45]. Copyright 2022, John Wiley and Sons.

4.1.1. Metal Nanoparticles in SPME

Metallic nanoparticles, particularly those containing metals such as silver and gold, have unique visual, physical, chemical, and biological properties that make them useful in a variety of applications. Their high affinity for both inorganic and organic mercury species enables them to be used efficiently in mercury extraction methods. These nanoparticles can also help separate heavy metals, organic chemicals (including pyrene, olefins, and methylene blue), and gaseous species (like NO and SO_2) [51]. Metal nanoparticles (MNPs) are crucial for the effective and selective extraction of analytes from various matrices. The application of metal nanoparticles in SPME has focused significantly on gold nanoparticles, due to the special properties they possess as an adsorbent material.

Gold Nanoparticles as Sorbent Material in SPME

Gold nanoparticles (AuNPs) are particularly notable due to their strong affinity for binding organic compounds with thiol groups and their effectiveness with other functional groups. AuNPs can spontaneously adsorb biomolecules containing thiol (SH) or amino (NH_2) groups, resulting in the formation of self-assembled monolayers. Despite their extensive surface area for interactions with analytes and column surfaces, research on AuNPs within separation science is limited. Their high surface-to-volume ratio, long-term stability, ease of synthesis, and favorable chemical modification properties make AuNPs promising candidates for diverse applications [48,52].

In a work by Wen et al., gold nanoparticles (AuNPs) were in situ coated on ordered mesoporous carbon (OMC) to generate an SPME covering with better extraction capacity and aniline selectivity. The researchers discovered that this composite significantly improved extraction efficiency, with enrichment factors for anilines ranging from 1143 to 3420, while such factors for alcohols and phenols ranged from 45 to 845 and 86 to 545, respectively, indicating notable aniline selectivity due to strong interactions between gold and amino groups. The approach quantified four anilines using gas chromatography and flame ionization detection, with limits of detection ranging from 0.072 to 0.18 μg/L and good precision (1.9% to 3.8% RSD). The technique was successfully applied to river and drinking water samples, with recoveries ranging from 83.9% to 107.7% for river samples and 94.0% to 113.1% for drinking water. The authors concluded that the AuNP/OMC composite fiber outperformed individual AuNPs, OMC, and commercial coatings in terms of extraction efficiency, emphasizing its potential for preconcentrating trace anilines in environmental samples and its strong affinity for thiol-containing compounds due to gold interactions [53].

In another study, Yang et al. developed a poly(3,4-ethylenedioxythiophene)@Au nanoparticle (PEDOT@AuNP) coating for SPME using a self-assembled monomer on AuNPs that was electropolymerized on stainless steel. They described the coating as having a cauliflower-like microstructure with exceptional heat stability (up to 330 °C) and durability, able to withstand over 160 extractions without losing performance. Because of its hydrophobic interactions with PEDOT and affinity for AuNPs, the coating has a high extraction capacity for polycyclic aromatic hydrocarbons (PAHs). The researchers used gas chromatography (GC) to obtain low detection limits (2.5–25 ng/L) and high repeatability, with recovery rates ranging from 89.9% to 112% in a variety of environmental water samples. Yang et al. found that the PEDOT@AuNP coating is an effective, long-lasting solution for PAH analysis in environmental settings [54].

An SPME coating based on gold nanoparticles was designed by Guitierrez et al. to detect organochlorine pesticides in ambient water samples. They explained that a layer-by-layer assembly method was used to apply the nanoparticles to SPME fibers, producing consistent coatings that were roughly 3 μm thick. Gallic acid or H_2O_2 was used as a reducing agent in the synthesis of the nanoparticles. Despite the thinner coating, the researchers observed that these fibers had detection limits as low as 0.13 μg/L and partition coefficients twice as high as those of commercial polyacrylate fibers. They also noted that after more than 100 extractions, the fibers showed good durability and repeatability, with relative standard deviation values ranging from 8.67% to 21.3% [55].

In conclusion, gold nanoparticles (AuNPs) are extremely versatile substances with proven physical and chemical characteristics that are available using established synthesis techniques. Because of their readily adjustable surface chemistry, they are very appealing for incorporation into a range of applications. AuNPs are now a popular option in academic research and an essential part of many industrial and point-of-care medical devices because of their qualities. They are perfect candidates for improving fiber coatings in the

context of SPME because of their high stability and adjustable surface characteristics, which will improve analyte adsorption and increase the technique's application in a variety of analytical problems [52].

Silver Nanoparticles as Sorbent Material in SPME

It is well known that silver ions can chemically combine with double-bonded molecules to produce strong interactions. In this interaction, electrons from the compound's π orbital are donated to the silver ion's empty s orbital, forming σ-bonds, and electrons from the silver ion's d orbital are formed from the compound's π* antibonding orbital. These chemical bonds are reversible, breakable at high temperatures, and stronger than van der Waals forces [56]. Silver chemistry has been studied in the creation of assisted transport membranes and stationary phases in chromatography (such as argentation chromatography), which are used to separate olefin/paraffin combinations [57,58].

Despite being more affordable than gold nanoparticles (AuNPs), there has been less research on the application of silver nanoparticles (AgNPs) as SPME coatings. Graphene oxide and polymers are combined as hybrid composites for the majority of AgNP applications, while the other components mostly drive extraction [59]. For SPME, other silver-based structures have also been investigated. These consist of electrodeposited silver dendrites, silver nanoplates or dendrites on copper wire supports, silver wires functionalized by sol–gel processes or conditioned by etching, and silver mirror coatings on stainless steel. To improve performance, these structures frequently need extra changes such as the use of polymer sheets [60–65].

Silver nanoparticles (AgNPs) made with glucose or gallic acid as reducing agents were used to develop a unique SPME coating, according to Gutiérrez-Serpa et al. They stated that a layer-by-layer technique was used to deposit the AgNPs onto stainless steel wires that had already been coated with a silver mirror, allowing for exact control over coating thickness. In close agreement with theoretical estimations, they observed that the coatings measured 3.2 μm thick for fibers prepared with gallic acid and 3.5 μm thick for fibers prepared with glucose. These fibers were used for the direct-immersion SPME-GC-FID analysis of sixteen polycyclic aromatic hydrocarbons (PAHs) in water, according to the scientists. They stressed that the AgNP fibers, especially those made with gallic acid, achieved remarkable analytical performance, including detection limits as low as 0.6 ng·mL^{-1}, RSDs below 26%, and durability for roughly 150 extraction/desorption cycles, despite the thinner coatings when compared to standard PDMS fibers. After testing the technique on environmental water samples that had been tampered with, they came to the conclusion that it worked well [59].

When compared to common macroscale materials like alumina, silver nanoparticles (Ag NPs) have garnered interest as sorbents in SPME because of their improved intrinsic features, such as greater chemical activity and ultrafine grain size. These nanoparticles can be chemically modified with particular reagents to create highly selective coatings for SPME fibers, which will enable the more effective and specific preconcentration and extraction of metal ions [52].

4.1.2. Metal Oxide Nanoparticles in SPME

Metal oxide nanoparticles (MONPs) are important in physics, chemistry, and materials research because of their various structural shapes and electrical characteristics, ranging from being insulators to being conductors. MONPs such as iron oxide, aluminum oxide, titanium oxide, and others are gaining popularity as efficient and cost-effective sorbents. Their nanoscale size results in a vast surface area and strong reactivity, making them excellent for removing heavy metals and dyes from aquatic environments. Furthermore, their functional

properties—which are influenced by factors including crystal structure, composition, and morphology—support a variety of pollution control applications, especially as ecologically friendly adsorbents in wastewater treatment [66–72]. Metal oxides are becoming more and more popular in chemical sensors and extraction materials, particularly for SPME, because of their excellent stability, adsorption capacity, and affordability. Environmental applications can benefit from the high surface-to-volume ratio and superior thermal stability of metal oxides such as cobalt oxide, titanium dioxide, lead oxide, zirconium oxide, and zinc oxide. Their special qualities, which change depending on their structure and content, make them very efficient sorbents.

TiO_2, Fe_3O_4, MnO_2, ZnO, and CuO are examples of metal oxide nanoparticles (MONPs) that are frequently employed in wastewater treatment to eliminate heavy metals and dyes. Their expanding relevance in pollution management and green chemistry solutions is highlighted by their usefulness for environmental remediation due to their photocatalysis, adsorption, and antibacterial action properties [45,66,73,74]. Subsequently, we will review some of these MONPs in detail.

Titanium Oxide Nanoparticles as Sorbents for SPME

The natural form of titanium, titanium dioxide (TiO_2), comes in three main crystal forms: brookite (which has a rhombohedral structure), metastable anatase (both of which have tetragonal structures), and stable rutile. The electrical structure, crystal form, size, shape, and any doping present influence the distinctive physicochemical characteristics of TiO_2 crystals [75]. It has been reported that TiO_2 nanotubes (TDNTs) possess notable qualities such as inertness, chemical and thermal stability, non-toxicity, low cost, durability, and corrosion resistance, making them highly suitable for various applications. These include environmental purification, photocatalysis, self-cleaning coatings, hydrogen generation and storage, gas sensing, biomedical uses, and electrode materials for solar cells. The structure of TDNTs is typically hydrogen titanate, with TiO_2 sheets rolled and separated by H+ ions, giving them a multi-walled, scroll-like appearance with large internal and external surfaces. These features make TDNTs ideal for use as sorbents. TiO_2, in various forms like nanowires, nanoparticles, and nanotubes, is a versatile and cost-effective material with significant potential in photocatalysis, electronics, and electrochemical systems, especially in analytical chemistry due to its high surface area and adsorption capabilities [14,76].

Anodized TiO_2 nanotube fibers were used by Shu et al. for in-headspace SPME in conjunction with gas chromatography–mass spectrometry (GC–MS) to identify volatile organic chemicals like xylenes (BTEX), benzene, toluene, and ethylbenzene. The research examined how the anodizing duration and annealing temperature affected the formation of TiO_2 nanotubes while maximizing the conditions for adsorption (time, ionic strength, and temperature) and desorption (time and temperature) for BTEX measurement. The technique showed linearity between 0.5 and 15,000 μg/L (R2 > 0.9954) and obtained detection limits for individual BTEX chemicals between 0.1 and 2.0 μg/L. The strategy demonstrated the potential of TiO_2 nanotube fibers as an efficient method for BTEX analysis by producing recoveries ranging from 92% to 97% when applied to actual samples [77].

Li et al. anodized titanium wire in ethylene glycol using NH_4F to create TiO_2-nanosheet-coated fibers for SPME. After extracting polycyclic aromatic hydrocarbons, phthalates, and UV filters using TiO_2 nanosheets that were roughly 1 μm long, 300 nm wide, and 80 nm thick, HPLC-UV detection was performed. With detection limits of 0.026–0.089 μg/L and calibration ranges of 0.1–400 μg/L, the fibers demonstrated excellent extraction efficiency and selectivity. With recoveries ranging from 88.8% to 107%, the technique reliably identified UV filters in environmental water samples and showed strong

repetition (4.50–8.76%) and reproducibility (7.75–9.64%). The fibers were repeatable, robust, and stable [78].

Iron Oxide Nanoparticles as Sorbents for SPME

The emergence of nanotechnology has revolutionized science by making it possible to create materials at the nanoscale (1–100 nm), which have special qualities because of their small size and high surface area-to-volume ratio. Iron oxide nanoparticles (IONPs) stand out among them due to their remarkable superparamagnetism, especially when they are between 2 and 20 nm in size. In the absence of an external magnetic field, this behavior, which is characterized by random variations in magnetization direction influenced by temperature and time (sometimes referred to as the Néel relaxation time), precludes net bulk magnetization. They are more magnetically susceptible than paramagnets, nevertheless, when exposed to a magnetic field. When designing and synthesizing IONPs for use, their magnetic behavior is crucial, especially in separation technologies where significant magnetization is necessary. Because of their easy surface modification, low cost of synthesis, and nanoscale property manipulation capabilities, iron oxide nanoparticles are widely used in various domains. They are also appropriate for biological applications due to their low toxicity, chemical inertness, and biocompatibility. Also, they are useful tools for environmental cleanup because of their enormous surface area, adaptability, and compatibility with adsorption technologies [79–82].

Iron oxide nanoparticles can take several forms, such as wüstite (FeO), ferrihydrite, goethite, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3), depending on their stoichiometry and oxidation state. Magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) have been extensively investigated for their distinct crystalline phases. Superparamagnetic iron oxide nanoparticles (SPIONs), particularly Fe_3O_4, are widely used in a variety of applications due to their ability to exhibit superparamagnetic properties when smaller than 20 nm [83]. Iron oxide nanoparticles and magnetite (FeO_4) are common magnetic materials used in water treatment because they provide a low-maintenance substitute for conventional adsorbents. FeO_4 nanoparticles are excellent nano-adsorbents for purifying wastewater, especially when functionalized, which improves their catalytic and adsorption capabilities. These nanoparticles are well known for their excellent adsorption capacity, stability, and reusability and can be readily recovered using an external magnetic field [84–87].

Ghiasvand et al. developed a new SPME fiber by embedding FeO_4/SiO_2 core–shell silica nanoparticles in polypyrrole (PPy) on stainless steel wire. Using direct-immersion (DI-) and headspace (HS)-SPME, this fiber was utilized to extract hexanal and heptanal from urine samples. GC-FID quantification was then performed. SEM and FT-IR were used to characterize the fiber, and important extraction parameters were refined. With detection limits of 0.1 and 0.5 ng/mL for hexanal and heptanal using HS-SPME-GC-FID and 0.1 and 1.0 ng/mL for DI-SPME-GC-FID, the calibration curves demonstrated good linearity (R2 > 0.99). The DI-SPME and HS-SPME replication studies had relative standard deviations of 6.5–6.6% and 5.1–5.3%, respectively. Urine samples without derivatization were successfully treated with both techniques; however, HS-SPME-GC-FID demonstrated better analytical performance and a longer fiber lifetime [88].

For the purpose of magnetic solid-phase extraction (MSPE) of organophosphorus pesticides (OPPs) from juice samples, Sereshti et al. fabricated a magnetic 3D graphene-iron oxide nanocomposite (3D-G-Fe_3O_4). This was followed by gas chromatography–nitrogen phosphorus detection (GC-NPD). Characterization of the 3D-G-FeO_4 was performed with SEM, FT-IR, and VSM. After optimizing key extraction parameters, low detection limits (1.2–5.1 ng/L) and excellent linearity (R2 = 0.9973–0.9999) were obtained. The

technique demonstrated good repeatability, with fruit juice OPP recovery rates ranging from 86.6% to 107.5%. GC-MS validation confirmed the findings, showing that the nanocomposite's 3D structure and magnetic characteristics gave it an exceptional extraction capability [40].

Manganese Oxide Nanoparticles as Sorbents for SPME

Manganese oxide, or MnO, is a common mineral that can be found in a variety of natural settings, including soil, silt, and aquifers. It frequently occurs as discrete particles, gels, or mixtures with other minerals like iron. MnO's special qualities allow it to potentially affect how pollutants behave in the environment through adsorption, photodegradation, and catalytic oxidation [89–91]. Manganese dioxide nanoparticles (MnO_2 NPs) have a vast surface area, strong oxidizing and adsorptive properties, and durability even in acidic environments. MnO_2 NPs are well known for their ability to effectively remove organic contaminants and heavy metals from water. They can be effectively separated using an external magnetic field because they are frequently boosted by magnetic compounds. These nanoparticles' chemical and physical interactions with polymers make them popular for removing dyes, and their supermagnetic characteristics make the separation process easier at ambient temperature. Through adsorption, ion exchange, and coprecipitation, MnO_2 also efficiently eliminates heavy metal ions [92,93].

Eskandarpour and Sereshti's study involved the electrospinning of manganese oxide (MnO) nanoparticles into a nanofibrous polycaprolactam (polyamide 6, PA6) coating. This coating was used as a novel fiber coating for the HS-SPME of specific phthalate esters (PEs) in water samples before GC-μECD analysis. Thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy, and SEM were used to characterize the coating. Important factors that affect the effectiveness of HS-SPME were optimized, such as extraction temperature, ionic strength, and extraction/desorption periods. The technique demonstrated a linear dynamic range of 0.500–500 ng/mL, limits of detection ranging from 0.0400 to 0.193 ng/mL, and relative standard deviations between 1.86% and 10.9% under these circumstances. The technique obtained relative recoveries of 90.3% to 107% when used on actual water samples, such as soda, river water, bottled water, and mineral water, proving its efficacy in identifying phthalate esters in a range of aqueous matrices [94].

Eskandarpour and Sereshti once more investigated the extraction and identification of carcinogenic nitrophenols (NPs), whereby contamination of soil and water poses serious health dangers. Using electrospinning, they created polyurethane–manganese oxide (PU-MnO) composite nanofibers and showed how effective they were in extracting mono-nitrophenols. Gas chromatography–microelectron capture detection (GC-μECD) in conjunction with a green HS-SPME technique used these nanofibers as adsorbents. The researchers obtained a linear dynamic range of 0.100–500 ng/mL, relative standard deviations (RSDs) of 2.53–11.2% (n = 3), and limits of detection of 0.0201 and 0.138 ng/mL after optimizing critical extraction parameters. Relative recoveries for river and wastewater samples using this approach ranged from 90.3% to 105%. The efficiency of the environmentally friendly analytical technique and PU-MnO nanofibers for identifying mono-nitrophenols in actual water samples was validated by the investigation [95].

Zinc Oxide Nanoparticles as Sorbents for SPME

The distinct electrical and optical characteristics of one-dimensional (1D) ZnO nanostructures, which result from their size and dimensionality, make them highly desirable. They are useful for basic research and as useful parts of nanodevices because of these characteristics. Their employment as interconnectors is also made possible by their 1D shape. Applications of 1D ZnO nanostructures demonstrate their versatility and promise

in cutting-edge technologies, including field-emission devices, gas sensors, UV photodetectors, solar cells, light-emitting diodes, and nanolasers [96,97]. More importantly, ZnO nanoparticles (NPs) are less expensive and easier to create than other nanomaterials. They can also be deposited on a wide range of substrates with precise and perfectly aligned orientations [98]. Also, all of these properties make them a good candidate in SPME fiber applications.

Duarte et al. studied the utilization of zinc oxide (ZnO)-coated glass fibers for assessing trihalomethanes (THMs) by HS-SPME-GC. Energy-dispersive X-ray spectroscopy and scanning electron microscopy were used to characterize the homogenous and porous ZnO layer that was applied on LiO–ZrO_2–BaO–SiO_2 glass fibers. To improve the analytical response, the study added 15% (*m*/*v*) salt and optimized the incubation (15 min), extraction (15 min), and desorption (10 min) periods. With dynamic ranges of 20–500 μg/L for trichloromethane, 15–250 μg/L for dichlorobromomethane and dibromochloromethane, and 10–100 μg/L for tribromomethane, the method showed excellent linearity for THMs in water. The reliability of the approach was confirmed by the fact that all compounds had correlation coefficients more than 0.9900 [99].

Additionally, Zhang et al. used a sol–gel technique to create a graphene-supported ZnO SPME fiber. ZnO was nucleated by graphite oxide (GO), and the resulting ZnO/graphene composite was integrated into a long-lasting sol–gel network. Adsorption sites were improved by the addition of graphene, which raised the BET surface area from 1.2 m^2/g to 169.4 m^2/g. With an enrichment ratio of 1087 for 1-octanethiol and less than 200 for non-sulfur compounds, the ZnO/graphene fiber demonstrated exceptional sensitivity and selectivity for sulfur compounds. It performed better than PDMS/DVB fibers and commercial PDMS. The fiber efficiently examined sulfur volatiles in Chinese chives and garlic sprouts when combined with GC-MS, achieving recoveries of 73.2–91.6%, RSDs of 3.6–9.1%, and detection limits of 0.1–0.7 μg/L [100].

While many metal oxide nanoparticles (MONPs) are suitable for SPME applications, this review concentrates on three of the most notable. Many other MONPs have significant features for this purpose, but we focused on a few to emphasize their distinctive contributions.

4.1.3. Carbon Nanoparticles in SPME

There are several different allotropic forms of carbon; the spherical C60 fullerene was the first to be discovered in 1985. Since then, other allotropes have been created or found, frequently by accident. Because of their exceptional electrical, mechanical, thermal, and adsorptive qualities, carbon nanotubes are the most often utilized of these for analytical reasons. Advanced materials such as fullerenes, carbon nanotubes, nanocones, and nanodiamonds have been used in the field of solid-phase extraction to provide analytical procedures that offer notable advantages over traditional approaches [19,101,102].

Carbon nanomaterials are popular nano-adsorbents in wastewater management due to their abundance, strong adsorption capabilities, cost-effectiveness, and high chemical and thermal stability. Activated carbon (AC), known for its high porosity and large surface area, has been a widely used adsorbent, though its cost drives the need for more economical options. As a result, alternatives such as graphene, carbon nanotubes (CNTs), carbon nitride (g-C_3N_4), and carbon dots have been explored for adsorption applications. The excellent regeneration potential of these nanomaterials further supports their use in contaminant removal from wastewater. Carbon-based nanomaterials like fullerenes and graphene, recognized by Nobel Prizes in 1996 and 2010, offer unique properties for a range of applications. Additionally, diverse carbon nanomaterials, including carbon nanoparticles, graphitic carbon nitride, ordered mesoporous carbon, and microporous carbon nanospheres, as shown in Figure 4 below, have been adapted as SPME fiber coatings [11,103,104].

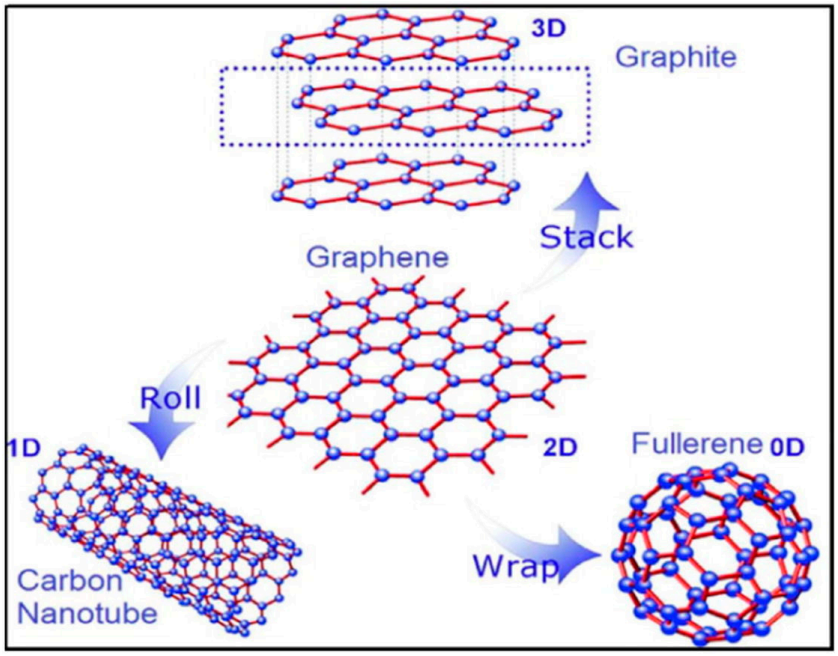


Figure 4. The basic building blocks of carbon nanomaterials. Printed with permission from [104]. Copyright 2020, Elsevier.

The structural conformation and hybridization state of carbon-based nanomaterials are intimately related to their electrical, chemical, and physical characteristics. The ground-state arrangement of the six electrons in carbon is $1s^2$, $2s^2$, and $2p^2$. Carbon can hybridize into sp, sp^2, or sp^3 configurations depending on its bonding with nearby atoms because of the promotion of an electron from the s orbital to an empty p orbital made possible by the tiny energy gap between the 2s and 2p shells. The higher energy of the promoted electron is offset by the energy obtained via covalent connections with nearby atoms. After taking into account the out-of-plane bonding from π bonds created by unhybridized p orbitals, this compensation is almost identical for both sp^2 and sp^3 hybridization [105,106]. The unique characteristics of these materials, including their high surface areas, large aspect ratios, and exceptional mechanical strength, along with excellent electrical and thermal conductivities, have led to a wide array of applications [107]. Carbon nanoparticles have been widely used as sorbent materials in SPME.

Carbon Nanotubes (CNTs) as Sorbent Materials in SPME

Considered tiny tubes made from rolled graphite sheets, carbon nanotubes (CNTs) come in two structural varieties: single-walled (SWCNTs) and multi-walled (MWCNTs). SWCNTs may range in length from hundreds of nanometers to several microns, with diameters usually between 1 and 10 nm. However, because MWCNTs are made up of numerous concentric cylinders held together by van der Waals forces, they have larger diameters, ranging from 5 nm to several hundred nanometers [108,109]. Sumio Iijima reported synthesizing a new carbon structure with needle-like tubes (carbon nanotubes) in 1991. These tubes were created using an arc-discharge evaporation procedure, which is similar to the synthesis of fullerenes [110].

Carbon nanotubes' extraordinary qualities open the door to new developments in engineering and research. In wastewater treatment and environmental monitoring, these materials offer a variety of uses for identifying and eliminating pollutants. CNTs are interesting options for SPME coatings because of their large adsorption area and high porosity. Their practical usefulness is further enhanced by their greater thermal and

physical stability as compared to traditional SPME coatings [108]. As stated above, CNTs have two structural forms, namely single-walled (SWCNTs) and multi-walled (MWCNTs).

Single-walled carbon nanotubes (SWNTs) are nanoscale tubes formed from a single rolled graphite layer, with diameters in the nanometer range and lengths reaching several micrometers, making them a prime example of one-dimensional materials. Because of the lack of mass and charge, photons are a great tool for studying and characterizing their unique structure [111,112].

Multi-walled carbon nanotubes (MWCNTs) are cylindrical nanostructures composed of sp^2 carbon. They have aspect ratios ranging from 10 to 10 million with diameters ranging from 3 to 30 nm and lengths up to several centimeters. MWCNTs are more rigid than single-walled nanotubes because of their multi-layered structure. They are also different from carbon nanofibers in that they have a hollow center, smaller exterior diameters, and a different wall structure [113].

Riboni et al. described a novel method for assessing aroma compounds in water that employs a recently developed SPME coating based on multi-walled carbon nanotubes (MWCNTs). They emphasized the use of helical MWCNTs as an excellent adsorbent because of their high extraction efficiency. The study used a desirability functions method to optimize extraction time and temperature, which improved the process's performance. The validation results show that this approach is very dependable for detecting analytes at ultra-trace levels, with detection limits ranging from 0.2 to 13 ng/L, good precision (relative standard deviations < 20%), and high recovery rates (80 ± 12% to 111 ± 11%) [114].

Rastkari et al. investigated the viability of using single-walled carbon nanotubes (SWCNTs) as an SPME adsorbent to detect monobutyltin, dibutyltin, and tributyltin in seawater. They stated that they adjusted key elements determining extraction efficiency, such as extraction and desorption time, temperature, and salinity. The approach showed linear calibration curves ($r > 0.992$) for concentrations ranging from 12 to 2000 ng/L, with detection limits < 5 ng/L, matching International Conference on Harmonization (ICH) criteria. They observed that, in comparison to commercial carboxen/polydimethylsiloxane fibers, the SWCNT fiber had greater heat stability (over 350 °C) and endurance, with a lifespan of more than 150 uses. They also stated that the procedure was successfully applied to Persian Gulf harbor seawater samples, where butyl tins were discovered, confirming SWCNTs' potential as a reliable SPME adsorbent for environmental analysis of butyltins in seawater [115].

Wang et al. developed a novel SPME method for analyzing polybrominated diphenyl ethers (PBDEs) in environmental samples that uses multi-walled carbon nanotubes (MWCNTs) as the fiber coating for gas chromatography with electron capture detection (GC-ECD). They found that the MWCNT coating had much larger enhancement factors (616–1756) than poly (5% dibenzene-95% dimethylsiloxane) (139–384) and activated carbon coatings (193–423). A 30 min extraction of a 10 mL sample yielded detection limits of 3.6–8.6 ng/L, with high linearity ($r^2 > 0.995$). They found great precision in peak area and retention duration at the 500 ng/L level, with relative standard deviations (RSDs) of 6.9–8.8% and 0.6–0.9%, respectively. The method was successfully applied to real samples such as local river water, wastewater, and milk. Their research revealed PBDE recoveries ranging from 90% to 119% for boosted samples. No PBDEs were found in river water or skimmed milk samples; however, they found PBDE levels of 134–215 ng/L in wastewater, 13–484 ng/L in whole fat milk, and 21 ng/L of BDE-47 in a semi-skimmed milk sample [116].

A study by Yazdi et al. examined the identification of ultra-trace amounts of polycyclic aromatic hydrocarbons (PAHs) in complex coffee and tea samples using hollow-fiber solid-phase microextraction (HF-SPME) in conjunction with high-performance liquid chromatography and UV detection (HPLC-UV). They clarified that for such matrices, HF-SPME

is a better option than direct-immersion SPME (DI-SPME), since DI-SPME offers little sample cleanup in intricate, "dirty" samples. According to Yazdi et al., the high porosity of the hollow fiber in HF-SPME enhances analyte selectivity and cleanup by preferentially adsorbing analytes from complicated mixtures. As the fiber sorbent, they created a new multi-walled carbon nanotube/zirconium oxide (MWCNT/ZrO_2) nanocomposite, which they attribute to hydrophobic interactions and π–π stacking for its high PAH adsorption. The technique produced low detection limits (0.033–0.16 μg L^{-1}) and a wide linear range (0.1–200 μg L^{-1}) with high precision (RSD < 6.6%). The authors concluded that the MWCNT/ZrO_2 HF-SPME approach is very effective for PAH analysis in complex matrices after reporting relative recoveries of 92.0–106.0% for PAHs spiked in water, coffee, and tea samples [117].

This section covered a variety of nanostructured materials, such as carbon-based nanoparticles, metal oxide nanoparticles, and metal nanoparticles, that can be employed as fiber materials in SPME. Because of their high surface area, structural adaptability, and superior adsorption capabilities, carbon-based nanomaterials—in particular, carbon nanotubes—have demonstrated superior performance among these. These materials are very promising for upcoming SPME applications since they offer improved extraction sensitivity and efficiency.

5. SPME Based on Nanocomposite Materials

Nanocomposites (NCs) are nanoscale materials made by combining organic and inorganic components, allowing them to incorporate each constituent's distinct features while also generating new functions to fulfill modern material demands. NCs, defined as having at least one component smaller than 100 nm, are solid structures with nanometer-scale spacing between phases. These materials can be made up of an organic matrix and an inorganic nanofiller, or vice versa, or from the hybridization of various organic and inorganic phases at different doping levels. NCs can contain nanoparticles (such as metal or silica), fibrous nanomaterials (such as nanofibers and nanotubes), and layered substances (such as graphite or layered silicates). NCs frequently outperform their individual components in terms of mechanical, electrical, optical, and catalytic qualities. NCs' multifunctional capabilities stem from more than just the sum of their components, with the high surface area-to-volume ratio playing an important role in their distinct structure–property relationships [118–121].

According to Bashtani et al., a nanocomposite composed of graphene oxide (GO), poly(methyl methacrylate) (PMMA), and FeO_4 nanoparticles was created specifically for the magnetic solid-phase extraction (MSPE) of aromatic amines. After coating magnetite nanoparticles with GO and PMMA, they created the composite (PMMA@GO-Fe_3O_4) and used SEM, TEM, XRD, VSM, and FTIR techniques to characterize it. Their results showed that the composite had preconcentration factors ranging from 139 to 173, successfully extracting amines including aniline and N,N-dimethylaniline. Along with precision with relative standard deviations ranging from 5.9% to 8.6%, they reported detection limits of 2–6 pg/mL. With recoveries of 90.3% to 99.0% when the technique was successfully applied to spiked water samples, its potential for environmental applications was demonstrated [122].

Farjaminezhad et al. used the sol–gel technique to create a superparamagnetic magnetite nanoparticle (SMNP) and polyethylene glycol (PEG) nanocomposite fiber, which chemically bonded the fiber to a silica surface that had been treated. According to their findings, 13 volatile organic compounds (VOCs) were successfully extracted from water samples using this new fiber. The fiber showed good thermal stability and a long lifespan by adjusting the mass ratio of SMNPs to PEG. According to Farjaminezhad et al.,

the SMNP/PEG fiber demonstrated a broad linear range (0.001–450,000 ng/L), lower detection limits (0.008–0.063 ng/L), and higher extraction efficiency when compared to commercial fibers made of polyacrylate (PA) and polydimethylsiloxane (PDMS). With intraday and interday accuracy ranging from 4.13 to 10.08% and reproducibility ranging from 7.35 to 14.79%, they found that this fiber had good repeatability and reproducibility. According to the authors, the fiber's longevity and chemical stability rendered it appropriate for use in gas chromatography–mass spectrometry (GC–MS) in conjunction with headspace solid-phase microextraction (HS-SPME) in VOC measurement. Its dependability in environmental applications was further proven by tests conducted on tap water, surface water, and groundwater [123].

Bagheri et al. reported the development of a zinc-based metal–organic framework/polyethersulfone (TMU-4/PES) nanocomposite coating on stainless steel wire for the headspace solid-phase microextraction (HS-SPME) of organophosphorous pesticides (OPPs) from environmental water and soil samples. They stated that the unique characteristics of the TMU-4/PES composite, including its high surface area, porous structure, and π–electron interactions from the PES polymer, contribute to a strong affinity for OPPs. After thermal desorption, OPPs were detected using gas chromatography with a nitrogen–phosphorus detector (GC-NPD). The authors noted the coating's simplicity, stability, and reusability, with up to 100 extraction cycles possible. Using a central composite design to optimize parameters, they achieved detection limits of 5–8 ng mL^{-1} for diazinon, fenitrothion, malathion, and chlorpyrifos. Bagheri et al. highlighted the method's effectiveness, demonstrating average repeatability and fiber-to-fiber reproducibility of 6.5% and 8.7%, respectively, and noted good recovery rates (88–108%) and reproducibility (5.9–10.1%) when applied to spiked environmental samples. The efficacy of the procedure was demonstrated by Bagheri et al., who observed good recovery rates (88–108%) and reproducibility (5.9–10.1%) when applied to spiked ambient samples, with average repeatability and fiber-to-fiber reproducibility of 6.5% and 8.7%, respectively [120].

Saraji et al. developed a mesoporous carbon–ZrO_2 nanocomposite coating on stainless steel wire as a novel SPME fiber, using direct carbonization of a Zr-based MOF without additional carbon sources. Optimized for BTEX analysis in water via GC-FID, the fiber showed excellent linearity (0.2–200 μg L^{-1}), low detection limits (0.05–0.56 μg L^{-1}), and high recovery (93–107%) with relative standard deviations of 3.5–6.7%. The study demonstrated its effectiveness in environmental analysis [38].

6. SPME Based on Nanoporous Structures

Porous structures are prevalent in nature, appearing in materials such as wood, cork, trabecular bone, and plant parenchyma. The invention of synthetic porous materials was a great leap in human civilization. Early examples included polymeric porous materials, termed "polymeric foams", with pore diameters exceeding 200 μm [124].

Nanoporous materials allow for selective adsorption depending on molecular configurations since their pores are similar in size to those of tiny molecules. For applications like fixed-bed devices that need good adsorption selectivity and capacity, zeolites—which are mostly made of silicon and oxygen—are perfect since they are plentiful, stable, and reasonably priced. Zeolitic imidazolate frameworks (ZIFs), covalent organic frameworks (COFs), and metal–organic frameworks (MOFs) are new types of nanoporous materials that provide substantial void volumes, great stability, and tunable, uniform cavities. In general, porous materials have interconnected voids that might or might not show three-dimensional translational repetition. As an illustration, consider porous silica frameworks (PSFs), porous organic frameworks (POFs), and layered double hydroxides (LDHs). Applications in adsorption, separation, and catalysis are driven by their wide gas–solid interfaces,

as demonstrated by solid foams, a simple porous system [125–127]. From conventional applications such as desiccants to more sophisticated ones, nanoporous materials have enormous potential in materials science. They function as size- and shape-selective reaction chambers for purification, which includes symmetric or asymmetric synthesis, heterogeneous catalysis, adsorption, and optical resolution of enantiomers. Modern technologies like chemical sensors, electrodes, data storage, imaging materials, and lasers are also using them more and more [128].

Overcoming difficulties in creating distinct phases at the nanoscale is necessary to fabricate nanoporous polymeric materials. Numerous methods have been devised, such as foaming, phase separation, molecular imprinting, microemulsion templating, and selective block removal in nanostructured copolymers. These techniques, which are frequently seen with scanning electron microscopy (SEM) and transmission electron microscopy (TEM), allow polymers to develop nanoscale porous architectures [124,129].

In general, pores fall into one of three shapes: slit, inkbottle, or cylindrical. They can be arranged to create 2D, 3D, crystalline, semi-crystalline, or amorphous structures. Analytes can be adsorbed by porous frameworks according to host–guest interactions (MOFs, POFs), anion exchange (LDHs), hydrophilicity (aluminosilicates), size (zeolites), or hydrophobicity (pure silica sieves) [125].

By functionalizing hexagonally ordered nanoporous silica (SBA-15) with 3-amino propyl triethoxysilane (APTES), Gholavind et al. reported creating a highly porous fiber covering a specialized solid-phase microextraction (SPME) apparatus for use in conjunction with gas chromatography–mass spectrometry (GC–MS) for the detection of trace levels of polycyclic aromatic hydrocarbons (PAHs) in water samples. Temperature, duration, ionic strength, and sonication were among the extraction parameters that were optimized, the researchers noted, one factor at a time. According to their findings, detection limits under ideal circumstances varied from 4.2 to 26.1 pg/mL, with relative standard deviations ranging from 3.3% to 7.7%. They also pointed out that the SPME fiber maintained a consistent extraction efficiency throughout 50 extractions, proving its robustness and appropriateness for environmental study [130].

Zhang et al. reported the effective synthesis of high-surface-area nanoporous carbon (NPC) using the metal–organic framework ZIF-90 as both a template and precursor, with furfuryl alcohol serving as a secondary carbon source. The resulting ZIF-90-NPC was applied to a stainless steel wire to form an SPME fiber. When combined with gas chromatography–microelectron capture detection (GC-μECD), the approach demonstrated large enhancement factors (984–2869), low detection limits (0.1–0.5 ng g^{-1}), and good linearity (0.3–50 ng g^{-1}) for detecting pyrethroid pesticides in fruits and vegetables. The RSDs for six replicate extractions ranged from 4.3% to 8.0%. The recoveries of spiked pesticides (5 ng g^{-1} and 20 ng g^{-1}) were between 86.0 and 104.0% and between 86.0 and 103.5%, with RSDs of 4.8–12.9% and 5.0–10.8%, respectively. The fiber performed consistently during 100 extraction cycles, with no notable loss of efficiency. The approach was successfully used to identify pyrethroids in fruit and vegetable samples [131].

According to Rahimi et al., CMK-3 nanoporous carbon was prepared and characterized as a highly porous fiber coating for solid-phase microextraction (SPME) that possesses an ordered carbon structure. According to their explanation, the material was immobilized onto copper, stainless steel, and platinum wires to produce new SPME fibers, with the copper–CMK-3 fiber exhibiting the best performance. The fiber was tuned for the gas chromatography–mass spectrometry (GC–MS) extraction of phenolic chemicals, the researchers observed. According to them, the following ideal conditions were achieved by applying a simplex optimization method: 13 mL sample volume, 56 °C extraction temperature, 7 min extraction time, 5.5 min ultrasonic duration, pH 5, and 8.9% salt concentration.

In comparison to a commercial product, Rahimi et al. demonstrated the fiber's selectivity for polar phenolic chemicals and observed higher extraction efficiency. They added that linear calibration curves with correlation coefficients above 0.99 and detection limits between 0.002 and 0.068 μg/mL were provided by the fiber. For at least 40 applications, the fiber's extraction effectiveness remained constant, and it was effectively used to examine phenolic chemicals in natural water samples [132].

7. Recent Advances in the Type of Fiber Material Used in SPME

In the food, environmental, and medicinal industries, solid-phase microextraction (SPME) is frequently used to preconcentrate and remove trace amounts of harmful and beneficial substances from natural goods. High efficiency, minimal resource use, ease of use, and speed are some of its main advantages. A key factor in improving extraction efficiency and selectivity is the sorbent material selection. Graphene (G), graphene oxide (GO), functionalized carbon nanotubes (CNTs), metal–organic frameworks (MOFs), covalent organic frameworks (COFs), molecularly imprinted polymers (MIPs), and other inorganic nanomaterials are all popular materials because of their large surface areas, tunable structures, high porosity, and chemical stability. Furthermore, because of their effectiveness and selectivity, environmentally friendly sorbents such as carbon black, aerogels, and zeolites have become more popular [133]. In this review, we did not look into MOFs as sorbent materials because the application of MOFs to SPME is another subject matter on its own, which we might look at separately in the future. Also, while MOFs have broad applicability, many suffer from water instability, degrading upon contact, which poses challenges for preparing water-based biological samples. Additionally, issues like recycling, waste management, and scalable production require further improvement [134].

In designing SPME fiber coatings, two key principles must be considered: the coating material should strongly and specifically interact with analytes to achieve effective enrichment, and it must be easily and securely immobilized on a supporting substrate. The evolution of SPME fiber coatings, as illustrated in Figure 5, highlights three key components: the coating material (blue dot), support material (green dot), and coating method (red dot). While the timelines show progress in certain areas, such as the shift from silica to metal fibers for better mechanical and chemical stability, other aspects have seen less development. The transition to metallic supports has improved the durability and lifespan of fibers due to their toughness and rigidity, replacing the more brittle silica fibers [45].

Han et al. demonstrated the progress of SPME fibers by creating a new substance specifically designed for the analysis of benzene series in oilfield wastewater. Through the use of an ionic liquid-assisted wet spinning process, metal–organic framework development, and pyrolysis, they modified graphene fibers with ordered mesoporous carbon nanotube arrays (CNTAs) to generate a unique fiber structure. Due to the crumpled graphene fiber stem and CNTAs acting as "hairs", the resulting "hair-brush-like" microfiber design greatly improves extraction efficiency. Verified by gas chromatography–mass spectrometry, this novel architecture provides a large surface area, a large number of binding sites, and remarkable enrichment capabilities for toluene, m-xylene, p-xylene, benzene, and ethylbenzene. In terms of extraction efficiency, the fibers outperformed commercial fibers thanks to their wide linear detection ranges (0.2–600 μg L^{-1}), low detection limits (0.005–0.03 mg L^{-1}), and exceptional repeatability (3.2–5.5% for one fiber, 2.1–6.7% for fiber-to-fiber) [39].

To measure nicotine and six metabolites in different parts of the rat brain, Zhang et al. developed a new hydrophilic–lipophilic SPME probe employing benzene diimine triazine benzodioxane–methylbenzodioxane (BDTB-MBD), a nitrogen-rich porous polymer coating. According to their findings, the coating material had balanced hydrophilic and hydrophobic qualities, a large surface area of 1001.7 m^2/g, an ideal pore diameter of 5.28 nm, and

outstanding stability. Ultra-high-performance liquid chromatography–triple quadrupole mass spectrometry (UHPLC-MS/MS) in conjunction with the SPME method produced high recovery rates (77.1% to 99.6%), low detection limits (0.002 to 0.020 μg L^{-1}), and wide linearity (0.01 to 100 μg L^{-1}). The investigation established the adsorption mechanism by revealing strong non-covalent interactions between BDTB-MBD and analytes. It effectively monitored the pharmacokinetics of nicotine in rat brain tissues, demonstrating its quick absorption, widespread distribution, and conversion to cotinine, nornicotine, and other metabolites. The researchers underlined that this strategy has uses in drug monitoring and neuroscience and provides a more effective and sensitive substitute for conventional techniques like solid-phase extraction [41].

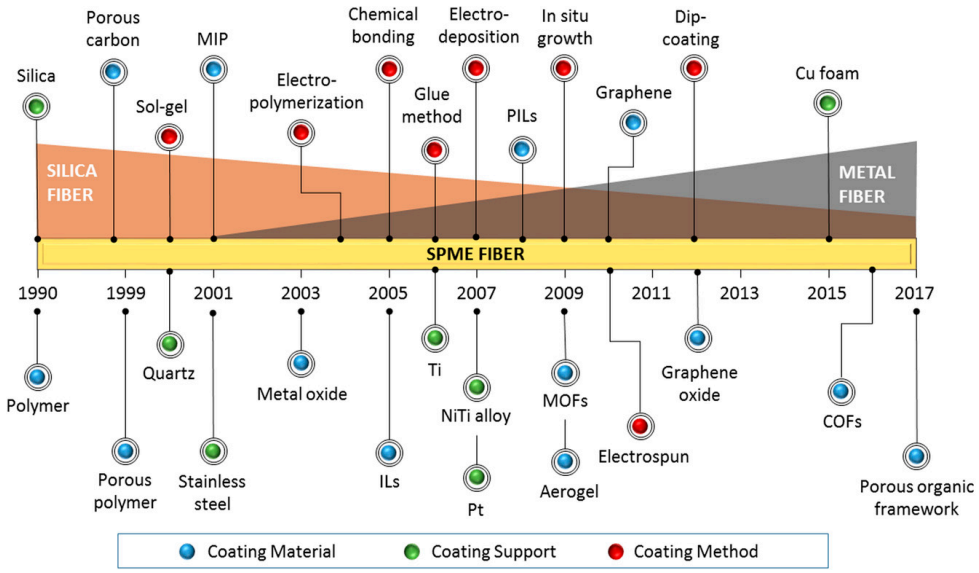


Figure 5. The timeline shows the main advancements in SPME fiber coatings, highlighting improvements in three areas: coating materials (blue dots), supporting materials (green dots), and coating methods (red dots). Printed with permission from [45]. Copyright 2022, John Wiley and sons.

For sensitive analyte detection, in-tube solid-phase microextraction (IT-SPME), which has become a popular and eco-friendly sample preparation method, is frequently used in conjunction with mass spectrometry or chromatography. This technique minimizes the usage of organic solvents, increases accuracy, and cuts down on analytical time. To improve enrichment efficiency, a variety of sorbent materials and extraction tools have been developed, including fiber-filled tubes, monolithic columns, sorbent-coated tubes, and particle-packed tubes. Although sample preparation is still difficult despite improvements in analytical equipment, solid-phase extraction has essentially supplanted conventional solvent-based techniques because of its ease of use and lower solvent use. To further reduce sample volume, minimize solvent use, and facilitate automation, microextraction techniques such as magnetic bead extraction, stir bar sorptive extraction, micro solid-phase extraction, and dispersive micro solid-phase extraction have been developed. All things considered, IT-SPME is a "green" technology that combines eco-friendly practices, online automation, and miniaturization [135,136].

8. Evaluation of Nanomaterial Performance in SPME

Table 2 summarizes the performance characteristics of a range of nanomaterials employed for use on SPME fibers.

Table 2. Evaluation of different types of nanomaterials and substrates employed in SPME fibers for the microextraction of different types of compounds and their detection efficiencies in detection devices.

Nanomaterial	Analyte	SMPE Substrate	Techniques	Number of Extraction Cycles	LOD	Linear Range	References
-	Butyltins and phenyltins	Polydimethylsiloxane (PDMS) fiber	GC-FPD	-	0.006–0.031 ng Sn l^{-1} for butyltins and 0.2–0.6 ng Sn l^{-1} for phenyltins	-	[37]
AuNPs/OMC	Aniline	Stainless steel wire	GC-FID		0.072–0.18 μg L^{-1}	0.1–1000 μg L^{-1}	[53]
PEDOT/AuNPs	Polycyclic aromatic hydrocarbons (PAHs)	Stainless steel wire	GC	160	2.5–25 ng L^{-1}	0.01–100 g L^{-1}	[54]
Helical MWCNTs	Fragrance materials	Bare fused silica fibers	GC-MS		0.2–13 22 ng/L		[114]
SWCNTs	Butyltins	Stainless steel wire	GC-MS	150	2–5 ng L^{-1}	6–2000 ng L^{-1}	[115]
MWCNTs	Polybrominated diphenyl ethers (PBDEs)	Fused silica fiber	GC-ECD	100	3.6–8.6 ng L^{-1}	28–2800 ng L^{-1}	[116]
MWCNT/ZrO_2	PAHs	Accurel Q polypropylene hollow fibers	HPLC-UV	5	0.033–0.16 g L^{-1}	0.1–200 g L^{-1}	[117]
CNTs/silica polymer	PAHs	Needle trap device (NTD)	Needle trap extraction (NTE) and GC-MS	3	0.001–0.01 ng mL^{-1}	0.01–20 ng mL^{-1}	[120]
PMMA@GO-Fe_3O_4	Aromatic amines	Fused silica	GC	139–173	2–6 pg mL^{-1}	0.007–100 ng mL^{-1}	[122]
Fe_3O_4/polyethylene glycol	Volatile organic compounds	Optical fiber	GC-MS	200	0.008–0.063 ng/L	0.001–450 × 104 ng/L	[123]
Hexagonally ordered nanoporous silica (SBA-15)	PAHs	Stainless steel wire	GC-MS	50	4.2 and 26.1 pg mL^{-1}.	-	[130]
ZIF-90 templated NPC (ZIF-90-NPC)	Pyrethroids pesticides	Stainless steel wire	gas chromatography-microelectron capture detection (GC-μECD),	100	0.1–0.5 ng g^{-1}	0.3–50 ng g^{-1}	[131]
CMK-3 nanoporous carbon	Polar phenolic compounds	Copper metal wires	GC-MS	40	0.002 to 0.068 g mL^{-1}	-	[132]
Pyrrole, carbon nanotubes, and titanium oxide (PPy-CNT-TiO_2)	Volatile aromatic compounds (BTEX)	Stainless stee wire	GC-FID	100	0.01 to 0.04 ng mL^{-1}	0.03–500 ng mL^{-1}	[137]

9. Conclusions and Future Perspectives in SPME

An important turning point in analytical chemistry was reached with the use of nanoparticles as fiber coatings in solid-phase microextraction (SPME). The sensitivity, selectivity, and reliability of extraction methods have been significantly enhanced by these cutting-edge materials, which include silica-based composites, metal–organic frameworks (MOFs), nanoporous carbons, and covalent organic frameworks (COFs). In environmental applications, the SPME method is frequently recommended for the extraction of several analytes. Due to their efficiency, NMs are a perfect substitute for traditional materials when it comes to the SPME of several analytes in environmental samples. Environmental sample SPME has made extensive use of nanomaterials (NMs), including polymer-based NMs, nanoparticles, nanofibers, nanoflakes, nanocomposites, nanorods, nanotubes, nanohorns, nanosheets, nanocubes, and nanospheres. Among these NMs' many benefits are their large specific surface area, strong catalytic activity, ease of synthesis, and favorable mechanical, electrical, optical, and physical characteristics [9].

As demonstrated by their capacity to endure numerous extraction cycles without suffering appreciable efficiency loss, nanomaterial-based fibers have exceptional stability, durability, and reusability. The use of novel functionalization methods has increased

their range of applications even more. Water, food, and environmental samples are just a few of the matrices to which these fibers can adapt effectively. They also function well in a variety of settings, including high ionic strengths, high temperatures, and when subjected to sonication. Furthermore, their selectivity for analytes—whether controlled by hydrophobicity, size exclusion, or host–guest interactions—highlights their adaptability and customized functionality for particular uses.

For the development of SPME devices, nanomaterials—particularly those produced via the bottom-up approach—offer significant cost advantages. For effective analyte extraction, this technique reduces material waste and permits the accurate fabrication of high-performance nanostructures. Its scalability facilitates mass production, which lowers manufacturing costs while improving the functionality of the gadget. The bottom-up method increases extraction efficiency and lowers material consumption by producing nanomaterials with high surface areas and regulated porosity, increasing the accessibility of SPME devices. In order to promote greener and more sustainable analytical techniques, these cost savings are essential for growing SPME applications in domains like environmental monitoring and medical diagnostics.

In the future, analytical science could undergo yet another revolution as nanomaterials and SPME are combined. Improved functionalization techniques and a wider variety of nanomaterials may result in fibers with higher resilience and specificity. Furthermore, the accuracy and sensitivity of analytical procedures will be further improved by developments in connecting these materials with cutting-edge detection systems like gas chromatography–mass spectrometry (GC-MS) or microelectron capture detection (μECD). A bright future for this area of study lies ahead of us as nanomaterial-based SPME fibers stand to be crucial in tackling new issues in food safety, pharmaceutical analysis, environmental monitoring, and other areas.

In conclusion, SPME research and development should focus more on promoting its use in a traditional laboratory and increasing its contribution to routine sample analysis or daily detection, even though the development of novel fiber coatings—particularly those with broad-spectrum applicability, high sensitivity, or exceptional selectivity for certain compounds—remains a key area of focus. This calls for the technology to be incorporated into higher education's teaching and practice system as a standard analysis method, becoming as well known as liquid-phase extraction and SPE. It also calls for ongoing product innovation and cost reductions based on the assurance of superior performance for the technology to become a standard piece of laboratory equipment and instrument. Nanomaterial coatings produced by robust processes involving fewer steps will prove appealing from a cost perspective. Furthermore, a key factor in encouraging the use of SPME technology is its application in the establishment of relevant national and industrial standard procedures [45].

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