Malaysian Journal of Analytical Sciences
(MJAS)
Published by Malaysian Analytical Sciences Society
ANALIS
Persatuan Sains Analisis Malaysia

A REVIEW ON APPLICATIONS OF GOLD AND SILVER-BASED SORBENTS IN SOLID PHASE EXTRACTION AND SOLID PHASE MICROEXTRACTION

(Satu Ulasan Penggunaan Pengerap Berasaskan Aurum dan Argentum dalam Pengekstrakan Fasa Pepejal dan Pengekstrakan Mikro Fasa Pepejal)

Wan Aini Wan Ibrahim[1, 2]*, Zetty Azalea Sutirman[1], Jawed Qaderi[1,3], Kasimu Abu Bakar[1,4], Siti Hajar Md Basir[1], Imad Eddine Aouissi[1]

[1]*Department of Chemistry, Faculty of Science*
[2]*Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research*
Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[3]*Department of Physical Chemistry, Faculty of Chemistry,*
Kabul University, 1001 Kabul, Afghanistan
[4]*Department of Chemistry, Faculty of Science,*
Sokoto State University, Sokoto, Nigeria

**Corresponding author: waini@utm.my, wanaini@kimia.fs.utm.my*

Received: 5 April 2020; Accepted: 7 June 2020; Published: August 2020

Abstract

Organic and inorganic pollutants and contaminants are considered harmful to ecosystem, even at low or trace-level concentrations. Several studies have been performed to degrade or remove these contaminants from environmental matrices and the use of pre-concentration approaches such as solid phase extraction (SPE) and solid phase microextraction (SPME) for their quantitation has been developed and showed great demand as an essential module to upgrade both practical efficiency and the analytical sensitivity. Gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) could be used as a sorbents prior to the combined high efficient separation or extraction methods with different detection techniques. Along with the rapid development of nanotechnology in material science, numerous nanomaterials include Au NPs and Ag NPs have been developed with particularly useful applications in analytical chemistry. Au NPs and Ag NPs are attracting a great deal of attention for their use in various technologies, including catalysis, optical and electronic devices, and separation science. In this review, recent progress of Ag NPs applied in SPE and SPME have been summarized and discussed. Au NPs and Ag NPs materials are evaluated for their unusual performance in various applications from environmental trace sample analysis to clinical investigations. Such great variety of uses makes nanomaterials kind of versatile tools in sample preparation for almost all categories of analytes.

Keywords: silver nanoparticles, gold nanoparticles, pre-concentration, solid phase extraction, solid phase microextraction

Abstrak

Bahan pencemar organik dan tak organik dianggap berbahaya kepada ekosistem, walaupun, pada kepekatan tahap rendah atau surih. Beberapa kajian telah dilakukan untuk nyahdegradasi atau penyingkiran bahan pencemar ini dari matriks sekitaran dan penggunaan pendekatan pra-pemekatan seperti pengekstrakan fasa pepejal (SPE) dan pengekstrakan mikro fasa pepejal (SPME)

untuk penentuan kuantitatif telah dibangunkan dan menunjukkan permintaan yang besar sebagai modul penting untuk meningkatkan kecekapan praktik dan sensitiviti analisis. Zarah nano emas (Au NPs) dan perak (Ag NPs) boleh digunakan sebagai pengerap sebelum gabungan pemisahan kecekapan tinggi atau kaedah pengekstrakan dengan teknik pengesanan yang berbeza. Seiring dengan perkembangan nanoteknologi yang pesat dalam sains bahan, banyak bahan nano termasuk Au NPs dan Ag NPs telah dibangunkan terutama aplikasi berguna dalam kimia analisis. Au NPs dan Au NPs menarik banyak perhatian untuk penggunaannya dalam pelbagai teknologi termasuklah pemangkinan, alat optik dan elektronik, dan sains pemisahan. Dalam tinjauan ini, kemajuan terkini Au NPs dan Ag NPs dalam SPE dan SPME dirumus dan dibincangkan. Bahan Au NPs dan Ag NPs dinilai untuk prestasi luar biasanya dalam pelbagai aplikasi dari analisis sampel surih alam sekitar kepada penyiasatan klinikal. Kepelbagaian penggunaan bahan nano menjadikannya sebagai peranti serba boleh dalam penyediaan sampel untuk hampir semua kategori analit.
.

Kata kunci: zarah-nano aurum, zarah-nano argentum, pra-pemekatan, pengekstrakan fasa pepejal, pengekstrakan mikro fasa pepejal

Introduction

Nanomaterials are a special kind of materials with nanometric scales in at least one dimension of their particles or pore structures, typically in the range of 1-100 nm [1]. Compared with conventional materials with micrometric or larger sizes, such limited scales endow nanomaterials with some exceptional and unprecedented properties in many aspects. Among them, the ultrahigh specific areas [2] and increasing surface activities facilitate the application of nanomaterials in sample preparation. In addition, tunable compositions, various morphologies and flexible functionalization offer a great number of opportunities in the development of novel nanomaterials for more efficient and versatile sample preparation. The qualitative and quantitative identification techniques of a large variety of complex and low volume samples based on using nanoparticles (NPs) as sorbents in various branches of analytical chemistry has been studying. Generally, NPs synthesis is conducted by either top-down or bottom-up procedures, which containing physical, chemical and biological methods (Figure 1). Their potential for sensing and biosensing has also been studied seriously for the detection of proteins, drugs, pesticides, and explosives. As such, the NPs have become desirable options for the development of pre-concentration techniques for trace-level chemical compounds from environmental matrices. The selectivity and sensitivity of analytical techniques have definitely been tremendously improved by using NPs as sorbents because of their advantageous properties (e.g. large surface area and specific affinity towards ultra-trace-level target analytes). At present, a large number of NPs (e.g. metallic and metal oxides, polymer-based nanocomposites, and silicon- and carbon-based NPs) have been incorporated in several sample preparation techniques for the proficient extraction and preconcentration of ultra-trace level chemical species before their determination by different analytical techniques. NPs have thus gained significant interest in the field of environmental science and technology, which includes the sampling and analysis of various organic pollutants. For soil and sediment samples, polymer-based nanosorbents have commonly been used for the determination of parabens, benzene homologues, and imidazolinones. For water samples, NPs such as metallic and mixed oxide NPs, have been introduced for a diverse of organic pollutants [3].

Gold nanoparticles (Au NPs) are gradually attracting a great deal of attention for their use in future technologies, including catalysis, optical materials, electronic devices, biosensors, drug carriers, and high contrast cell imaging. On the other hand, Au NPs have been widely used in analytical procedures because of their size dependent electrical properties, high electrocatalytic activity, and functional compatibility with molecules and polymers. Besides, biomolecules containing thiol (SH) or amino (NH_2) groups can be adsorbed spontaneously on to gold surfaces to generate well-organized, self-assembled monolayers. Although Au NPs provide a large surface area to interact with column surface and analyte, very little research has been dedicated to understanding their impact on separation science. Additionally, Au NPs are characterized by a high surface-to-volume ratio, long-term stability, easy synthesis and favourable chemical modification [4].

The application of silver nanoparticles (Ag NPs) has been gradually increasing in nano-functionalised consumer products. Ag NPs are among the most commonly used in the fields of textiles, medical devices, dentistry, wound healing, cosmetics, water filters, water disinfection, paints, food industries and electrical appliances due to its antimicrobial activities, the unique physicochemical properties and high surface-to-volume ratio [5]. The rapid development and increase use of Ag NPs has given rise to their release into the environment and has possible toxic effects on living organisms such as plants, fish and humans [6]. The toxicity of Ag NPs is generally believed to be related with their release of Ag ions, which have toxic effects on many pathogens.

Nowadays there are various analytical options available for the extraction and pre-concentration of trace levels of organic pollutants based on the integration between different kinds of nanomaterials and various types of extraction techniques which includes solid phase extraction (SPE), magnetic solid phase extraction (MSPE), solid phase microextraction (SPME), and stir bar sorptive extraction (SBSE). These techniques are being used for the quantitative analysis on different forms of analytes in environmental samples such as volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, pharmaceuticals, and other endocrine disrupting chemicals. As a result, the use of these innovative pre-treatment approaches has become crucial for the identification and quantitation of many pollutants [3].

The challenge in speciation analysis of organic and inorganic pollutants and contaminants deals with sample preparation techniques for separation prior to determination. Solid phase extraction (SPE) and solid phase microextraction (SPME) are promising approaches for the separation of these pollutants based on gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) [7]. SPE and SPME are also a widely-used sample preparation technique for the extraction of pesticides and ions due to their high extraction efficiency, little consumption of organic solvent, low cost and easy operation. According to Zhao et al. [6], in view of the low concentration of target species and complex sample matrix in the real-world samples, the novel non-chromatographic separation techniques such as cloud point extraction, liquid phase microextraction and SPE and LPME methods are good choices for real sample analysis, which can not only separate analytes of interest, but also remove sample matrix and pre-concentrate target species. To date, there are numbers of publications on applications of Au and Ag NPs, but only few of them reported on their application, individually in separation and extraction area [8-11]. Therefore, the present review specifically describes the application of both Au and Ag NPs as well as their derivatives in extraction techniques for analysis of various analytes. It also summarizes the published works from the year of 2011 to 2019.

Sorptive extraction techniques

Solid-phase extraction (SPE) is progressively a suitable sample preparation technique. It is used either to pre-concentrate or to purify analytes of interest from a great variety of sample matrices [12]. SPE is used for extracting and pre-concentrating trace-level organic impurities from environmental matrices. This technique developed in the 1980s and ever since then, it has confirmed to be the most dominant tool for the isolation and purification of target analysis [13]. The advantages of SPE include simplicity, flexibility, high selectivity, automation, rapidity, higher enrichment factors, and the absence of emulsion and use of different sorbents [14]. The extraction efficiency of SPE has been significantly improved by the combination of NPs, which afford more trapping sites than previous sorbents. Compared with other liquid extraction techniques for organic pollutants, NPs-based SPE provides lower detection limits for a wide variety of organic pollutants with minimal sample and solvent volumes [3].

SPME was introduced for the first time as sample separation technique by Belardi and Pawlizyn [15].

SPME consists of fused silica coated with a polymeric stationary phase where the partition equilibrium between the analytes and the stationary phase occurs. This solvent free method has undergone a rapid development [16] owing to the fact that SPME is environmentally friendly and able to do multiple operations in a single step (sampling, extraction, pre-concentration and sample introduction) [17]. SPME has been applied in various research areas, from environmental chemistry [18] to biomedical analysis [19, 20]. Besides, being solvent free, this method is rapid and selective [21]. It can also be coupled with various separation techniques and analytical technologies such as gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) [22], high performance liquid chromatography (HPLC) [23], HPLC-mass spectrometry (HPLC-MS) [24] and capillary electrophoresis (CE) [25]. Although the SPME technique has various advantages, the fiber that is available in the market has serious drawbacks such as the fiber of the stationary-phase does not chemically bond well with the coating material, the commonly used fibers are quite thick and lack stability at high temperatures [26]. In recent years, these problems are being solved by developing a new coating protocol [3]. In the literature there are examples of sorbent particles that lower the accumulated amount of analyte [27], which achieve large errors if analyte concentrations are determined on the basis of calibration with non-complexing standards. To evaluate the utility of SPME for the analyte, it will be necessary to develop a thorough understanding of how the sample components can influence the SPME measurement of a specific target molecule or species.

The rather high cost of SPME coatings does not allow their use for many applications. Moreover, the available commercial coatings are not suitable for a wide range of analytes. Some features such as the ease of coating procedure, ability to extract the specific target analyte(s), cost and (chemical, mechanical and thermal) stability must be taken into account for the applied materials as SPME coatings. Recently, nanomaterials have attracted a great importance as new fiber coatings because of their excellent properties better than conventional polymeric coatings used in SPME [28]. Au NPs possess several interesting properties such as long-term stability, high surface-to-volume ratio, ease of chemical modification and compatibility with biomolecules [29]. In addition, molecules with functional group such as thiol (–SH) or amino (–NH_2) groups can be adsorbed onto the Au surface to form a well-organized self-assembled monolayer (SAM), and this flexibility has attracted great attentions and has been widely used in sample pre-concentration and separation science [30]. The overview of the whole procedures to determine various pollutants from different samples can be shown in Figure 2.

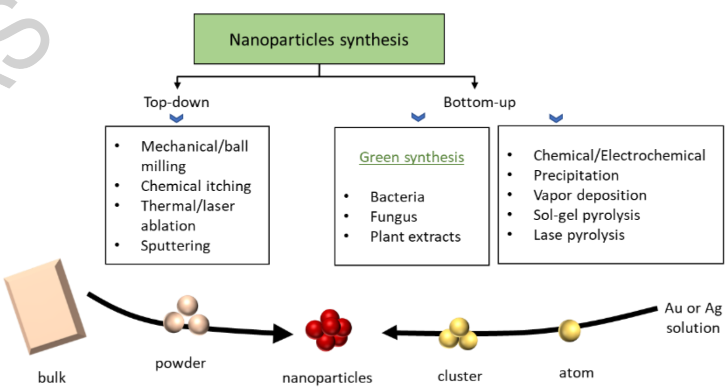

Figure 1. Different approaches for nanoparticles synthesis

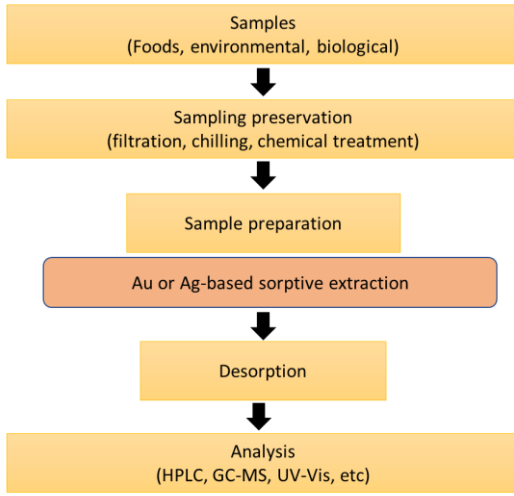

Figure 2. General procedures for determination of various pollutants in different samples using Ag or Au-based extraction techniques

Gold nanoparticles

In ancient times, gold was still considered a way to improve health. In fact, Chinese and Indian cultures have used many gold compounds in the form of "Swarna Bhasma" to treat various health problems, such as improving the vital power and male ineffectiveness [29]. The exceptional properties of this element, such as inertness, nontoxic nature towards cell and biocompatibility, make it an attractive material for many researchers in biological and medical applications. It is also considered an important material for use in therapy and imaging [31]. Au NPs have unique optoelectronic properties and the way that they interact with the light produces vibrant colors which have been used for centuries by artists, and have been further developed into advanced applications like organic photovoltaics, sensory probes, therapeutic agents, drug delivery in biological and medical applications, electronic conductors and catalysis [29, 31]. It is worth noting that by varying the size, shape and surface textures, or aggregation state of Au NPs, we can adjust different optical and electronic properties. Besides to these applications, in earlier 1978s, scientists found that it can also be used as an antitumor agent which can open a new investigation gate to be deeply explored [32]. Au NPs tend to resonantly absorb and scatter visible light and infrared light during the excitation of surface plasmon oscillation. By studying the distance dependent scattering properties of the Au NPs, it has been found that it is possible to detect biological events at the single molecular level. This finding was used for bio-sensing [33]. Au NPs publications has magnificently increased in various fields including biological fields which according to Chen et al., this development is related to the increase in nanotechnology field that increased the governmental awareness and funding, and fast evolution in synthetic chemistry molecular biology. On the one hand to recent developments in the field of nanotechnology, which has increased government awareness and funding, and on the other hand to the rapid evolution in synthetic molecular biology chemistry [34].

Au NPs can be synthesized by reduction of gold salts in the presence of stabilizing agents which role is to prevent their agglomeration. They can be prepared by using physical, chemical, and supercritical fluid technology methods. The tendency of Au NPs to absorb and scatter visible and near infrared light resonantly, facilitate the production of Au NPs by physical methods like microwave irradiation, sonochemical method, ultraviolet radiation, laser ablation, thermolytic process and photochemical process [32]. These methods have proved a good adaptation for the production of nanoparticles. As for the chemical methods, they are based on the production of Au NPs using chemical reactions such as the synthesis of Au NPs in an aqueous medium using citrate or sodium borohydride as the reducing agent. It has been reported in the literature that the synthesis of small and uniform size of Au NPs can be achieved by controlling the concentration of citrate [35]. One of the most important advantages of Au NPs, is that they can be effectively altered by functionalizing their monolayers by thiol linkers. The modification can be performed by proteins, nucleic acids, oligosaccharides, and peptides [36-38]. Another way to produce Au NPs is using an inorganic matrix as a support or host. In fact, Mukherjee et al. have used silica supported surface which contains silanol groups. These allow the reduction of chloroaurate ion to Au NPs [39].

Au NPs have unique properties such as special stability, multiple surface functionalities, and great biocompatibility [8]. The physical properties of Au NPs are inertness, nontoxicity and the tendency to absorb and scatter visible and near infrared (NIR) light resonantly. Au NPs are versatile materials for a broad range of applications with well characterized electronic and physical properties due to well-developed synthetic procedures. In addition, their surface chemistry is easy to modify. These features have made Au NPs one of the most widely used nanomaterials for academic research and an integral component in point-of-care medical devices and industrial products worldwide [32].

Silver nanoparticles

Ag NPs play an important role in nanoscience and nanotechnology and their application have been gradually increasing in nano-functionalized consumer products. Ag NPs are among the most commonly used in the fields of textiles, medical devices, dentistry, wound healing, cosmetics, water filters, water disinfection, paints, food industries and electrical appliances due to its antimicrobial activities, the unique physicochemical properties and high surface-to-volume ratio [5].

Peculiar properties of Ag NPs, they have been used for several applications, including as antibacterial agents, in industrial, household, and healthcare-related products, in consumer products, medical device coatings, optical sensors, and cosmetics, in the pharmaceutical industry, the food industry, in diagnostics, orthopedics, drug delivery, as anticancer agents, and have ultimately enhanced the tumor-killing effects of anticancer drugs. Nano-sized metallic particles of Ag NPs are unique and can considerably change physical and chemical properties which include optical, electrical, and thermal, high electrical conductivity, and biological properties due to their surface-to-volume ratio; therefore, these nanoparticles have been exploited for various purposes [40, 41].

The determination of heavy metals at trace levels is one of the most important targets of analytical chemists because of their roles in our life. Although some trace metals such as cobalt are essential to human whose daily requirement is only a few milligrams, however, it can be harmful to human health if ingested in high level. Therefore, the elemental composition of trace metals is important to ensure the water and food quality. Furthermore, the metal content in water, sediment, plants and animals can also provide essential information on the levels of contamination in the environment [42].

Physical and chemical properties of Ag NPs including surface chemistry, size, size distribution, shape, particle morphology, particle composition, coating/capping, agglomeration, dissolution rate, particle reactivity in solution, efficiency of ion release, cell type, and finally type of reducing agents used for synthesis are crucial factors for determination of cytotoxicity [43]. The smaller size particles of Ag NPs could cause more toxicity than larger, because they have larger surface area. Shape is equally important to the determination of toxicity. Ag NPs toxicity mainly depends on the availability of chemical and or biological coatings on the nanoparticle surface [41].

In the past decade, nano-scale solid materials including Ag NPs have become very important due to their unique chemical and physical properties including high chemical activity and adsorption capacity to many element ions onto the surface of the nanomaterials. The surface atoms are unsaturated and subjected to combination with other element ions by static electricity for which the nanoparticles can adsorb element ions with good adsorption speed. Ag NPs have been utilized as sorbent due to their improved intrinsic properties such as chemical activity and fine grain size compared with the macro-scaled classical substances such as normal scale titanium dioxide, alumina, etc. Nanoparticles were chemically modified by a reagent to obtain a new selective solid phase extractant for the pre-concentration of metal ions [42].

Sample preparation based on gold nanoparticles

Gold nanoparticles in solid phase extraction technique

Au NPs are the main metal nanomaterials for bio-separation and analysis of pesticides and organic contaminants due to their excellent physical and chemical properties, providing an excellent surface for recognizing target molecules. Gong *et al*. developed a sensitive enzymeless Au NPs decorated graphene nanosheets (GNs) sensor to separate organophosphate pesticides (OPPs) in solid phase extraction (SPE) [43]. Such a nanostructured composite film, combining the advantages of Au NPs with two dimensional GNs, intensely enabled the enrichment of nitroaromatic OPPs onto the surface and recognized their stripping voltammetric exposure of OPPs by choosing methyl parathion (MP) as the model analyte. The stripping voltammetric routines of seized MP were assessed by cyclic voltammetric and square-wave voltammetric analysis. The combination of the nanoassembly of Au NPs-GNs, SPE, and stripping voltammetry provided a fast, simple, and sensitive electrochemical method for detecting nitroaromatic OPPs. The stripping analysis is highly linear over the MP concentration ranges of 0.001 - 0.1 $\mu g/L$ and 0.2 - 1.0 $\mu g/L$, with a detection limit of 0.6 $\mu g/mL$. This designed enzymeless sensor exhibited good reproducibility and acceptable stability [43].

Photo luminescent amino functionalized graphene quantum dots (GQDs-amino) associated with Au NPs was made in the determination of kanamycin sulfate that the Au NPs were produced by the reduction of $AuCl_4$ with $NaBH_4$ in an aqueous dispersion of graphene quantum dots (GQDs-amino) also containing the cationic surfactant cetyltrimethylammonium bromide (CTAB). The Au NPs-GQDs-amino-CTAB system showed a suppressed photoluminescence that was amplified in the presence of kanamycin. Under optimized experimental conditions, the photoluminescence amplification of the nanomaterial system showed a linear response as a function of kanamycin concentration, covering three orders of magnitude (10^{-7} to 10^{-5} mol/L). The use of SPE with a cartridge packed with aminoglycoside selective molecularly imprinted polymer ensured selectivity in determinations made on yellow-fever vaccine and veterinary pharmaceutical formulations. The analytical results were statistically similar to those obtained with an HPLC based fluorescence method. The proposed method was a simple, sensitive and selective approach that did not involve the use of toxic reagents employed for chemical derivatization of aminoglycoside antibiotics [44].

Gold/polypyrrole (Au-PPy) nanocomposite coated silica is a novel sorbent described for the efficient SPE of common microcystins (MCs) well below the recommended United States EPA and World Health Organization (WHO) guidelines. With the optimized SPE protocol, samples spiked with MCs were determined at ng/L concentrations by liquid chromatography mass spectrometry (LC–MS) in different aqueous sample matrices, including HPLC-grade, tap, and lake water which indicated excellent extraction efficiency and reproducibility. The Au-PPy nanocomposite coated sorbent material was reusable for at least three independent MC extractions with a single SPE cartridge in the concentration range of 10 - 500 ng/L. Therefore, the Au-PPy nanocomposite coated silica sorbent is a promising new material for the quantification of MC variants in water samples [45].

Silver (Ag) and gold (Au) NPs impregnated in nylon membrane filters were capable of being used as a new sorbent for SPE of small amounts of Hg from natural waters [47]. This sorbent had a large surface area of

NPs and thus contributed to high efficiency of adsorption of Hg from aqueous phase to membrane filters. A Zeeman mercury analyzer RA–915+ helped in thermal desorption of Hg from membrane filters which eliminated the sample preparation step sharply reducing the risk of contamination. The LOD for the determination of Hg in water using Ag-Au NPs impregnated in nylon membrane filters was around 0.4 ng/L which was much lower than 200 ng/L achieved by cold vapour generation technique. This convenient sorbent obviously showed the potential which could be applied to remove Hg in water samples with appropriate results. Additionally, water samples could be sampled directly to the impregnated filters from water forms thus decreasing contamination during transport and storage [46].

Nowadays Au NPs coated silica sorbent with ionic liquid (Au NPs-IL-silica sorbent) has been productively prepared and applied for the pre-concentration of sulfonylurea herbicides (SUHs) in water samples [4]. Different factors that influenced pre-concentration efficiency, such as pH of the sample and elution conditions, were optimized. It was confirmed that pH was a critical variable in the adsorption process of the SUHs onto the recommended sorbent. On the other hand, this sorbent helped to achieve good recoveries and precisions in terms of repeatability and reproducibility by SPE. Better recoveries and lower LODs and LOQs were obtained when the Au-NP–IL–silica sorbent was used, although its synthesis was longer due to the addition of the IL. In addition to this, the use of the Au-NP–IL-functionalized silica sorbent as SPE material is in some cases, a better option than the use of conventional SPE materials such as C18 sorbents. The use of these types of materials could be expanded to the extraction of other compounds for clean-up/pre-concentration processes prior to a chromatographic or electrophoretic separation method [4].

In addition, gold nanoclusters (Au NCs) immobilized paper has been developed for the detection and determination of zinc (Zn) in whole blood and cells. A headspace (HS)-SPE method was used for the separation of Zn and a visible fluorescence from the Au NCs coated paper was quenched by ZnH_2 produced from hydride generation (HG). By using X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT), the potential mechanism for the detection of zinc was studied. This new sorbent increased selectivity of the HS-SPE method because the zinc hydride was effectively separated from sample matrices by hydride generation. A limit of detection of 3 $\mu g/L$ Zn^{2+} and a relative standard deviation (RSD, *n* = 7) of 2% were obtained using a commercial fluorescence spectrophotometer as the detector. In visual detection, a very low amount of Zn^{2+} in biological sample was simply distinguished from the blank with the bare eye. The above mentioned sorbent had several unique benefits, which contributed in straight forward, rapid, affordable and equipment-free HS-SPE technique for visual detection [47]. Table 1 lists some of the applications of Au NPs-based SPE for extracting organic pollutants prior to analysis.

Gold nanoparticles in solid phase microextraction technique

Organic hydrophobic compounds are present in water in low concentrations, and they can be analyzed by means of a pre-concentration method using sorptive extraction techniques such as SPME. In the last decades, organic-inorganic hybrid materials have received considerable attention because they can combine the advantages of organic and inorganic materials to some extent [52]. Some hybrid materials, especially the hybrid nanomaterials, are considered to be high-efficiency sorbents due to their high specific surface area, and excellent thermal and mechanical stability [47]. Similarly, a novel poly(3,4-ethylenedioxythiophene)@Au nanoparticles (PEDOT@AuNPs) hybrid coatings were prepared and characterized.

First, the monomer 3,4-ethylenedioxythiophene was self-assembled on AuNPs, and then electropolymerized on a stainless steel wire by cyclic voltammetry. The obtained PEDOT@AuNPs coating was rough and presented micro-structure with thickness of ~40 µm. It displayed high thermal (up to 330 ℃) and mechanical stability and could be used more than 160 times in SPME without losing extraction performance. The coating showed high extraction capacity for many pollutants such as naphthalene, 2-methylnaphthalene, acenaphthene, fluorene and phenanthrene, due to the hydrophobic interaction between the analytes and PEDOT and the additional physicochemical affinity between polycyclic aromatic hydrocarbons and Au NPs. The SPME-GC method was successfully applied for the determination of three real samples, and the recoveries for standards added were 89.9 - 106% for lake water, 95.7 - 112% for rainwater and 93.2 - 109% for soil saturated water [53].

In order to improve the SPME performance, a novel SPME fiber coating was fabricated by direct hydrothermal growth of titanium (Ti) and nickel oxide composite nanosheets (NiOCNS) on a NiTi wire (NiTi–TiO_2/NiOCNSs). Modification of the TiO_2/NiOCNSs coating was carried out by electrodeposition of Au NPs with potentiostatic technology. The extraction performance of the Au NPs modified TiO_2/NiOCNSs coated NiTi (NiTi–TiO_2/NiOCNSs-Au NPs) fiber was evaluated using polycyclic aromatic hydrocarbons (PAHs), phthalate acid esters (PAEs) and chlorophenols (CPs). The results obtained indicated that the novel fiber exhibited excellent extraction efficiency and good selectivity for PAHs. Relative recoveries varied from 86.3% to 104%. Furthermore, the novel fiber could be fabricated in a highly reproducible manner and had a high stability and long life span [28].

In a similar report, a novel fiber coating based on electrodeposition of Au NPs onto stainless steel followed by self-assembled 1, 8-octanedithiol coating were developed. This novel fiber resulted in high surface area with floccular structure and was found to be capable and selective towards some polychlorinated biphenyls (PCBs), UV filters, CPs and PAHs. The different selectivity for all UV filters was due to the weak polarity for alkyl chain on the coating surface. Furthermore, the fiber was more stable and durable than the commercially available PDMS and PA coated fibers by being able to maintain its performance when getting immersed into organic solvents and can be used up to 200 times [54].

The excellent physical and chemical properties of carbon nanomaterials have made them promising materials to be used as SPME fiber coatings. Among them, graphene oxide (GO) also has some properties such as long term stability and a huge surface area, and thus has great potential as a sorbent material in SPME [55]. Graphene-coated SPME fibers have also been reported [56]. However, the stable structure of graphene has limited potential application as a fiber coating. Au NPs decorated GO coating was studied intensively and the nanomaterials of GO and Au NPs were used successfully as fiber coating absorbents. The novel Au NPs decorated GO-coated SPME fiber was prepared through layer by layer (LBL) self-assembly process of GO and a self-assembled monolayer process between the thiol (–SH) and Au NPs. Effects of the adsorption and desorption factors were investigated systematically. The single fiber repeatability (RSDs = 1.9 - 6.5%) and fiber-to-fiber reproducibility (RSDs = 4.3 - 9.2%) were both satisfactory.

The analysis of ten aromatic hydrophobic organic compounds (HOCs) in two real water samples (running water and snow water) showed satisfactory results using Au NPs/GO SPME fiber. The inherent chemical stability of Au and GO makes the novel Au NPs/GO SPME fiber having high stability and durability towards acid, alkali and organic solutions, and high temperature. A novel SPME fiber based on a stainless steel wire coated with Au nanoparticle decorated GO was reported [1]. The extraction performance of the fiber was tested with aromatic hydrophobic organic chemicals as the model analytes. The fiber showed excellent extraction efficiency, good mechanical strength, and good stability in acid, alkali and organic solutions, and under high temperature. The relative standard deviations for the single fiber repeatability and fiber-to-fiber reproducibility were less than 6.90 and 16.87%, respectively. Compared with GO SPME fibers and Au nanoparticle SPME fibers, the Au NPs/GO fiber has lower detection limits (≤ 60 ng/L) and a better linear range for all analytes. Correlation coefficient values were between 0.9958 and 0.9993. The as-established SPME-GC-FID method was successfully used for two real natural samples, and recovery of the analytes ranged from 82.65% to 126.06%.

Table 2 lists some of the applications of Au NPs-based SPME for extracting organic pollutants prior to analysis. Comparing the work of Zare et al. [16] and Liu et al. [59] on PAHs using HPLC-UV for water samples showed that the work by Zare et al using SAM of Au-NPs gives a much lower LOD compared to the use of gold-coated fiber.

Table 1. Summary of different Au NPs-composite sorbent employed in SPE techniques for extraction of organic and inorganic pollutants in environmental samples

Sorbent	**Analyte**	**Matrix**	**Linear Range**	**RSD (%)**	**LOD**	**Recovery (%)**	**Detection Technique**	**Ref.**
Au NPs-GNs	Organophosphates (Ops)	Methyl parathion (MP)	0.001 - 1.0 µg/L	5.6 (n=10)	0.6 ng/L	96.2 - 105.0	UV-Vis	[43]
Au NPs-GQDs-amino-CTAB	Kanamycin sulphate	Yellow fever vaccine	$2.5 \times 10^{-7} - 1.0 \times 10^{-5}$ mol/L	1.2 - 1.7	6.0×10^{-8} mol/L	96.7 ± 2.1	HPLC-FLD	[44]
rGO/Au composite	Microcystins (MCs)	Milk	0.05 - 200 ng/L	2.0 - 14.9	≤1.5 ng/L	94.1 - 103.2	UHPLC-MS/MS	[48]
Ag/AuNPs-impregnated in nylon membrane filters	Hg	Water	5 - 500 ng/L	-	0.4 ng/L	100± 2	Zeeman Mercury analyzer RA–915+	[46]
AuNPs-PPy nanocomposite	Microcystins (MCs)	Water	2.5 - 80.0 ng/L	1.6 - 5.4 (n=3)	≤1.5 ng/L	94.1 - 103.2	LC-ESI–MS	[45]
Au-NP–IL–silica	Sulfonylurea herbicides (SUHs)	Water	0.05 - 1.00 mg/L	4.5 (n=10)	0.002 - 0.009 µg/L	83.9 - 105.0	CLC–DAD	[4]
Au NPs-PDMS	Hg(II)	Environmental water	0.2 - 1.0 µg/L	2.24 - 6.21	70 µg/L	97.5 - 101.7	ICP-MS	[49]
(SPCE/PEDOT: PSS/Au NPs/1-m-4-MP)	Tyramine (4-hydroxyphenethyl amine)	Spiked serum	5 - 100 nM	2.73 (n=3)	2.31 nM	93.6 - 102.4	CE-NMR	[50]

Table 2 (cont'd). Summary of different Au NPs-composite sorbent employed in SPE techniques for extraction of organic and inorganic pollutants in environmental samples

Sorbent	Analyte	Matrix	Linear Range	RSD (%)	LOD	Recovery (%)	Detection Technique	Ref.
Au@Ag nanostructure based SERS substrate	Acetamiprid (AC)	Matcha tea	1.0×10^{-5} - 1.0×10^{3} µg/L	<4.85 (n=5)	2.63 $\times 10^{-5}$ µg/g	99.85 - 115.60	GA-PLS-DFT	[51]
Paper immobilized BSA–Au NCs	Zinc, Zn^{2+}	Whole blood and cells	1 - 200 µg/L	2 (n=7)	3 µg/L	95 - 102	ICP-MS	[47]

GNs, graphene nanosheets; GQDs, graphene quantum dots; CTAB, cetyltrimethylammonium bromide; PPy, polypyrrole; PDMS, polydimethylsiloxane; SPCE/PEDOT: PSS/Au NPs/1-m-4-MP, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate gold nanoparticles 1-methyl-4- mercaptopyridine modified screen-printed carbon electrode; BSA, bovine serum albumin; SERS, surface-enhanced Raman scattering

Table 3. Summary of different Au NPs-composite sorbent employed in SPME techniques for extraction of organic and inorganic pollutants in environmental samples

Sorbent	Analyte	Matrix	Linear Range	RSD (%)	LODs	Recovery (%)	Detection Techniques	Ref
Poly (3,4-ethylenedioxythiophene) @Au nanoparticles (PEDOT@AuNPs)	Naphthalene, 2-methyl-naphthalene, acenaphthene, fluorene and phenathrene)	Lake water (LW), rainwater (RW) and soil saturated water (SSW)	0.01-100 µg/L	1.1 - 4.0 and 5.8 - 9.9	2.5 - 25 ng/L	89.9 - 106 (LW) 95.7 - 112 (RW) 93.2 - 109 (SSW)	GC-FID	[53]
SAM of 1,8 - octanedithiol onto AuNPs coating via Au-S bonding (C8–S–AuNPs/SS fibers)	UV filters	Environment-al water	0.10 - 400 µg/L	3 - 9.4	0.025 - 0.056 µg/L	92.0 - 106.0	HPLC-UV	[54]
Cedar-like AuNPs (AuNPs/SS)	Phthalate esters and aromatic hydrocarbons	River water under Bapanxia bridge	0.05 - 300 µg/L	03.82 - 5.19	0.008-0.037 µg/L	97.00	HPLC-UV	[57]

Table 4 (cont'd). Summary of different Au NPs-composite sorbent employed in SPME techniques for extraction of organic and inorganic pollutants in environmental samples

Sorbent	**Analyte**	**Matrix**	**Linear Range**	**RSD (%)**	**LODs**	**Recovery (%)**	**Detection Techniques**	**Ref**
Porous Ag@Au)	Nitrofurazone and (NFZ) Semicarbazide (SCA)	Aqueous solution	0.1- 5.0 nmol/L (NFZ) and 0.1- 7.0 nmol/L (SCA)	4.4 (NFZ) and 5.3 (SCA)	2.7 nmol/L 6.4 nmol/L		Surface enhanced Raman spectroscopy	[58]
AuNPs Modified TiO_2/NiOCNSs coated NiTi fiber (NiTi–TiO_2/NiOCNSs-AuNPs)	Organic solvents (methanol, tetrahydrofuran, Chloroform and dimethylsulfoxide)	River water, rainwater, Wastewater	0.05 - 350 µg/L	5.2- 7.5	0.012-0.053 µg/L	95.4–103	HPLC-UV	[28]
SAM of Au-NPs	Polycyclic aromatic hydrocarbons (PAHs)	Environmental water	1 - 500 ng/mL	<5.1	0.10-0.89 ng/mL	84- 106	HPLC/UV	[16]
Au NPs/ GO/SPME fiber	Aromatic Hydrophobic organic chemicals (HOCs)	Ultrapure water	0.05 - 300 µg/L	16.87	10- 50	82.65-126.06	GC-FID	[1]
Gold-coated fiber	PAHs	Water	0.20 - 500 µg/L	2.03-11.7	0.016 - 0.22 µg/L	86.0-112.9	HPLC-UV	[59]
AuNPs coated fiber	2-hydroxy-4-ethoxybenzophenone (BP-3) 2-ethylhexyl-4-methoxycinnamate (EHMC), 2-ethylhexyl-4-(*N*,*N*-dimethylamino) benzoate (OD-PABA) and 2-ethylhexyl salicylate (EHS)	River water	0.004 - 200 µg/L	1.91 - 4.20	0.43 - 570 ng/L	77.9 and 108	HPLC-UV	[60]
AuNPs	organochlorine pesticides (OCPs)	Water	100 - 500 µg/L	8.67-21.3.	0.04-0.41 µg/L	85.0-97.1	GC–ECD	[61]

SAM, self-assembled monolayer; NiOCNs, nickel oxide composite nanosheets; OD-PABA, octyl-dimethyl-para-aminobenzoic acid

Table 5. Summary of different Ag NPs-composite sorbent employed in SPE techniques for extraction of organic and inorganic pollutants in environmental samples

Sorbent	Matrix	Analyte	LOD	RSD (%)	Coefficient of Determination (R^2)	Detection Technique	Ref.
Impregnated nylon membrane filter AgNPs	Natural water	Mercury, Hg	0.4 ng/L	7.9	0.9989	ETAAS	[46]
AgNPs coated silica gel-ammonium pyrrolidine-dithiocarbamate (APDC)	Tap and sea water	Lead, Pb	0.36 ng/mL	<10.0	0.95	FAAS	[66]
1-(2-pyridylazo)-2-naphthol (PAN)-AgNPs	Natural water	Co(II)	0.78 µg/L	3.1	0.992	AAS	[42]
CS-AgNPs	Lake water	Al(III), Cd(II), Cu(II), Co(II), Fe(III), Ni(II), Pb(II), Zn(II)	0.001 - 0.1 µg/L	7.0 -12.0	0.92 - 0.98	ICP-MS	[63]
Ag-SiO_2-PDPA	Pesticides	Lindane, Diazinon, Fenthion, Ethion, Piperonyl-butoxide, Fenoxaprop-*p*-ethyl	0.02 - 0.05 µg/L	6.0-10.0	0.983-0.999	GC-MS	[64]
AzS@AgNDs	Water	HEX, DES, DIS, BPA	0.1 - 5.0 pg/mL	2.8 - 6.0	0.991-0.995	UPLC-MS/MS	[65]

PVIM-MNPs, poly(1-vinylimidazole) functionalized magnetic nanoparticles; UMPs, unmodified magnetic particles; GMPs, glutathione-functionalized magnetic particles; DMPs, dopamine-functionalized magnetic particles; Mix D–G, mixture of GMPs and DMPs; Ag-SiO_2-PDPA, silver nanoparticles-doped silica-polydiphenylamine; HEX, hexestrol; DES, diethylstilbestrol; DIS, dienestrol; BPA, bisphenol

Table 6. Summary of different Ag NPs-composite sorbent employed in SPME techniques for extraction of organic and inorganic pollutants in

Sorbent	**Analyte**	**Matrix**	**Linearity**	**RSD (%)**	**LOD**	**Recovery (%)**	**Detection Technique**	**Ref.**
Ag nanocomposite	Parabens	Water/Beverages	0.05−200 µg/L	2.4 - 3.1 and 3.4 - 4.2 (n=3)	0.01 µg/L	25−28	HPLC/UV	[73]
Ag nanodendrites and PDMS/PEG	Volatile Aldehydes	Edible Oils	−	7.5 - 11.2 (n=3)	0.5 - 0.2 µg/L	56.7−86.3	GC-MS	[75]
Ag NPS decorated graphene oxide	PAHs	Water Sample	0.02 - 50 µg/L	8.6 - 17.5	2 - 10 ng/L	84.4−116.3	GC-FID	[76]
Porous Ag fiber	Organotin compounds	Textile	1.0 - 5.0 nmol/L	−	0.2 ppb	−	Raman Spec.	[77]
Dendritic AgN structure	UV filters	Water Sample	0.3 - 400 µg/L	5.7 - 8.7	0.05 - 0.12 µg/L	85.5−105.5	HPLC-UV	[68]
Graphene coated Ag NPs	Bisphenol A	Water Sample	2 - 100 µg/L	14 and 13	1 µgL	97-110	Raman Spec.	[78]
Ag NPs aggregate	PAHs	Water sample	−	3.85 - 96.98	7.56 x 10^{-10} M	95-115	Raman Spec.	[69]
Ag NPs	MUFAMES	Food sample	0.2 - 0.9 mg/kg	< 5.2	< 5.2 µg/kg	86.6−96.1	HPLC	[72]
Ag NPs	PAHs	Water Sample	−	< 25	0.6 ng/L	86.3−105	GC-FID	[71]
AgNPs@MCM-14	Capecitabine	Plasma Sample	25 - 1000 µg/L	1.3 and 13.3	−	87 - 105	CE−UV	[79]

PDMS, polydimethylsiloxane; PEG, polyethylene glycol; MUFAMEs, monounsaturated fatty acid methyl esters

Conclusion

Au and Ag NPs and its functionalized forms are attracting a great deal of interest because of their wide applications in sorptive SPE and SPME techniques for the analysis of trace-level organic pollutants from various environmental matrices. The integration of Au NPs, Ag NPs, polymers, and nanocomposite materials with SPE and SPME has produced tremendous improvements in analytical performance. Analytical merits such as sensitivity, reproducibility, repeatability, and reusability were greatly improved by integrating Au NPs and Ag NPs and its functionalized form with SPE and SPME for trace level analytes. The Au NPs an Ag NPs themselves have recently emerged as powerful separation materials when their surfaces are modified with appropriate chemical species because Au NPs and Ag NPs-based separation materials are easy to produce and modify. Thus, we believe that analytical systems incorporating Au NPs and Ag NPs will be an important part of future investigations into the applications of nanotechnology in separation science. Functionalization of gold and silver nanoparticle is an effective strategy for the generation of highly selective and sensitive sorbent materials for many kinds of targets. There is great demand for the design and development of new functionalized Ag and Au nanomaterials with better specificity and selectivity for the various applications possible in analytical chemistry in food, drugs, and as sensors.

Acknowledgment

We would like to express our thanks to the Ministry of Education (MoE) and Universiti Teknologi Malaysia (UTM) for the award of the Professional Development Research Grant (PDRU grant number Q.J130000.21A2.04E12)) to ZAS. JQ is grateful for the scholarship awarded by the Higher Education Development Program (HEDP), Ministry of Higher Education and Kabul University, Afghanistan and KAB would like to thank the Petroleum Technology Development Fund, Nigeria for the postgraduate scholarship.

References

1. Xu, L., Qi, X., Li, X., Bai, Y. and Liu, H. (2016). Recent advances in applications of nanomaterials for sample preparation. *Talanta*, 146: 714-726.
2. Wu, W., Zhang, C. and Yang, S. (2017). Controllable synthesis of sandwich-like graphene-supported structures for energy storage and conversion. *New Carbon Materials*, 32(1): 1-14.
3. Azzouz, A., Kailasa, S. K., Lee, S. S., Rasc, A. J., Ballesteros, E., Zhang, M. and Kim, K. (2018). Review of nanomaterials as sorbents in solid-phase extraction for environmental samples, *Trends in Analytical Chemistry*, 108: 347-369.
4. Simo, E. F. and Zougagh, M. (2013). Use of gold nanoparticle-coated sorbent materials for the selective preconcentration of sulfonylurea herbicides in water samples and determination by capillary liquid chromatography, *Talanta,* 105: 372-378.
5. Anekthirakun, P. and Imyim, A. (2019). Separation of silver ions and silver nanoparticles by silica based-solid phase extraction prior to ICP-OES determination. *Microchemical Journal*, 145: 470-475.
6. Zhao, B., He, M., Chen, B., and Bin, H. (2018). Ligand-assisted magnetic solid phase extraction for fast speciation of silver nanoparticles and silver ions in environmental water. *Talanta*, 183: 268-275.
7. Mwilu, S. K., Siska, E., Baig, R. B. N., Varma, R. S., Heithmar, E. and Rogers, K. R. (2014). Separation and measurement of silver nanoparticles and silver ions using magnetic particles. *Science of the Total Environment,* 472: 316-323.
8. Liu, F. K. (2009). Analysis and applications of nanoparticles in the separation sciences: A case of gold nanoparticles. *Journal of Chromatography A*, 1216: 9034-9047.
9. Lin, J. H. and Tseng, W. L. (2012). Gold nanoparticles for specific extraction and enrichment of biomolecules and environmental pollutants. *Reviews in Analytical Chemistry*, 31: 153-162.

10. Dastafkan, K., Khajeh, M., Ghaffari-Moghaddam, M. and Bohlooli, M. (2015). Silver nanoparticles for separation and preconcentration processes. *TrAC-Trends in Analytical Chemistry*, 64: 118-126.
11. Oliveira, E., Núnez, C., Santos, H. M., Fernández-lodeiro, J., Fernández-lodeiro, A., Capelo, J. L. and Lodeiro, C. (2015). Revisiting the use of gold and silver functionalised nanoparticles as colorimetric and fluorometric chemosensors for metal ions. *Sensors & Actuators: B. Chemical*, 212: 297-328.
12. Ten-Doménech, I., Martínez-Pérez-Cejuela, H., Lerma-García, M. J., Simó-Alfonso, E. F. and Herrero-Martínez, J. M. (2017). Molecularly imprinted polymers for selective solid-phase extraction of phospholipids from human milk samples. *Microchimica Acta*, 184(9): 3389-3397.
13. Erger, C., and Schmidt, T. C. (2014). Disk-based solid-phase extraction analysis of organic substances in water. *Trends in Analytical Chemistry*, 61: 74-82.
14. Dimpe, K. M., and Nomngongo, P. N. (2016). Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices. *Trends in Analytical Chemistry*, 82: 199-207.
15. Belardi, R. and Pawliszyn, J. (1989). The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. *Water Quality Research Journal*, 24(1): 179-191.
16. Zare, F., Ghaedi, M., and Daneshfar, A. (2015). The headspace solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental water samples using silica fiber modified by self-assembled gold nanoparticles. *Analytical Methods*, 7(19): 8086-8093.
17. Arthur, C. L., and Pawliszyn, J. (1990). Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry*, 62(19): 2145-2148.
18. Sadowska-Rociek, A., Surma, M. and Cieślik, E. (2014). Determination of polycyclic aromatic hydrocarbons in coffee and coffee substitutes using dispersive SPE and gas chromatography-mass spectrometry. *Food Analytical Methods*, 8(1): 109-121.
19. Pincemaille, J., Schummer, C., Heinen, E. and Moris, G. (2014). Determination of polycyclic aromatic hydrocarbons in smoked and non-smoked black teas and tea infusions. *Food Chemistry*, 145: 807-813.
20. Serrano, M., Bartolome, M., Gallego-Pico, A., Garcinuno, R. M., Bravo, J. C. and Fernandez, P. (2015). Synthesis of a molecularly imprinted polymer for the isolation of 1-hydroxypyrene in human urine. *Talanta*, 143: 71-76.
21. Li, L. and Leopold, K. (2012). Ligand-assisted extraction for separation and preconcentration of gold nanoparticles from waters. *Analytical Chemistry*, 84: 4340-4349.
22. BorFuh, C., Yang, Y. C., Tsai, H. Y. and Ho, L. S. (2003). Solid-phase microextraction coupled with gas chromatography and gas chromatography-mass spectrometry for public health pesticides analysis. *Chromatographia*, 57(7): 525-528.
23. Eisert, R., and Pawliszyn, J. (1997). Automated in-tube solid-phase microextraction coupled to high-performance liquid chromatography. *Analytical Chemistry*, 69(16): 3140-3147.
24. Wu, J., Tragas, C., Lord, H. and Pawliszyn, J. (2002). Analysis of polar pesticides in water and wine samples by automated in-tube solid-phase microextraction coupled with high-performance liquid chromatography-mass spectrometry. *Journal of Chromatography A*, 976 (1-2): 357-367.
25. Fang, H., Liu, M. and Zeng, Z. (2006). Solid-phase microextraction coupled with capillary electrophoresis to determine ephedrine derivatives in water and urine using a sol-gel derived butyl methacrylate/silicone fiber. *Talanta*, 68(3): 979-986.
26. Lashgari, M. and Yamini, Y. (2019). An overview of the most common lab-made coating materials in solid phase microextraction. *Talanta*, 191: 283-306.

27. Guo, M., Gong, Z., Allinson, G., Tai, P., Miao, R., Li, X. and Zhuang, J. (2016). Variations in the bioavailability of polycyclic aromatic hydrocarbons in industrial and agricultural soils after bioremediation. *Chemosphere*, 144: 1513-1520.
28. Wang, H., Zhang, Y., Zhang, M., Zhen, Q., Wang, X. and Du, X. (2016). Gold nanoparticle modified NiTi composite nanosheet coating for efficient and selective solid phase microextraction of polycyclic aromatic hydrocarbons. *Analytical Methods*, 8(31): 6064-6073.
29. Daniel M. C. and Astruc, D. (2004). Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Review*, 104: 293-346.
30. Sykora, D., Kasicka, V., Miksik, I., Rezanka, P., Zaruba, K., Matejka, P. and Kral, V. (2010). Application of gold nanoparticles in separation sciences *Journal of Separation Science,* 33(3): 372-87.
31. Boisselier, E. and Astruc, D. (2009). Gold nanoparticles in nanomedicine: preparations, imaging, diagnostics, therapies and toxicity. *Chemical Society Reviews,* 38(6): 1759-1782.
32. Khan, M. S., Vishakante, G. D., and Siddaramaiah, H. (2013). Gold nanoparticles: A paradigm shift in biomedical applications. *Advances in Colloid and Interface Science*, 199-200: 44-58.
33. Sönnichsen, C., Franzl, T., Wilk, T., von Plessen, G., Feldmann, J., Wilson, O. and Mulvaney, P. (2002). Drastic reduction of plasmon damping in gold nanorods. *Physical Review Letters*, 88(7): 077402.
34. Chen, H., Roco, M., Li, X. and Lin, Y. (2008). Trends in nanotechnology patents. *Nature Nanotechnology*, 3(3): 123-125.
35. Mandal, T., Fleming, M. and Walt, D. (2002). Preparation of polymer coated gold nanoparticles by surface-confined living radical polymerization at ambient temperature. *Nano Letters*, 2(1), 3-7.
36. Lévy, R., Thanh, N. T. , Doty, R. C., Hussain, I., Nichols, R. J., Schiffrin, D. J., Brust, M., and Fernig, D. G. (2004). Rational and combinatorial design of peptide capping ligands for gold nanoparticles. *Journal of American Chemical Society*, 126(32): 10076-10084.
37. Schofield, C. L., Haines, A. H., Field, R. A. and Russell, D. A. (2006). Silver and gold glyconanoparticles for colorimetric bioassays. *Langmuir*, 22(15): 6707-6711.
38. Skidmore, M. A., Patey, S. J., Thanh, N. T. K., Fernig, D. G., Turnbull, J. E. and Yates, E. A. (2004). Attachment of glycosaminoglycan oligosaccharides to thiol-derivatised gold surfaces. *Chemical Communications*, (23): 2700-2701.
39. Mukherjee, P., Patra, C. R., Ghosh, A., Kumar, R. and Sastry, M. (2002). Characterization and catalytic activity of gold nanoparticles synthesized by autoreduction of aqueous chloroaurate ions with fumed silica. *Chemistry of Materials*, 14(4): 1678-1684.
40. Chernousova, S. and Epple, M. (2013). Silver as antibacterial agent: Ion, nanoparticle, and metal. *Angewandte Chemie International Edition*, 52: 1636-1653.
41. Zhang, X. F., Liu, Z. G., Shen, W. and Gurunathan, S. (2016). Silver nanoparticles: Synthesis, characterization, properties, applications, and therapeutic approaches. *International Journal of Molecular Sciences*, 17(9): 1534-1568.
42. Khajeh, M. and Sanchooli, E. (2011). Synthesis and evaluation of silver nanoparticles material for solid phase extraction of cobalt from water samples. *Applied Nanoscience,* 1: 205-209.
43. Gong, J., Miao, X., Zhou, T. and Zhang, L. (2011). An enzymeless organophosphate pesticide sensor using Au nanoparticle-decorated graphene hybrid nanosheet as solid-phase extraction. *Talanta*, 85: 1344-1349.
44. Toloza, C. A. T., Almeida, J. M. S., Khan, S., Yasmin, G., Andrea, R., Romani, E. C. and Aucélio, R. Q. (2018). Gold nanoparticles coupled with graphene quantum dots in organized medium to quantify aminoglycoside anti-biotics in yellow fever vaccine after solid phase extraction using a selective imprinted polymer. *Journal Pharmaceutical and Biomedical Analysis,* 158: 480-493.

45. Devasurendra, A. M., Palagama, D. S. W., Rohanifar, A., Isailovic, D., Kirchhoff, J. R. and Anderson, J. L. (2018). Solid-phase extraction, quantification, and selective determination of microcystins in water with a gold-polypyrrole nanocomposite sorbent material. *Journal of Chromatography A*, 1560: 1-9.
46. Panichev, N., Kalumba, M. M. and Mandiwana, K. L. (2014). Solid phase extraction of trace amount of mercury from natural waters on silver and gold nanoparticles. *Analytica Chimica Acta*, 813: 56-62.
47. Huang, K., Dai, R., Deng, W., Guo, S., Deng, H. and Wei, Y. (2018). Gold nanoclusters immobilized paper for visual detection of zinc in whole blood and cells by coupling hydride generation with headspace solid phase extraction. *Sensors And Actuators B: Chemical*, 255: 1631-1639.
48. Jiang, K., Huang, Q., Fan, K., Wu, L., Nie, D. and Guo, W. (2018). Reduced graphene oxide and gold nanoparticle composite-based solid-phase extraction coupled with ultra-high-performance liquid chromatography-tandem mass spectrometry for the determination of 9 mycotoxins in milk. *Food Chemistry*, 264: 218-225.
49. Hsu, K., Lee, C., Tseng, W., Chao, Y. and Huang, Y. (2014). Selective and eco-friendly method for determination of mercury(II) ions in aqueous samples using an on-line AuNPs-PDMS composite microfluidic device/ICP-MS system, *Talanta*. 128: 408-413.
50. Li, Y., Hsieh, C., Lai, C., Chang, Y., Chan, H., Tsai, C., and Wu, L. (2017). Biosensors and Bioelectronics Tyramine detection using PEDOT: PSS/AuNPs/1-methyl-4- mercaptopyridine modified screen-printed carbon electrode with molecularly imprinted polymer solid phase extraction. *Biosensors and Bioelectronic*, 87: 142-149.
51. Hassan, M. M., Li, H., Ahmad, W., Zareef, M., Wang, J., Xie, S., Wang, P., Ouyang, Q., Wang, S. and Chen, Q. (2019). Au@Ag nanostructure based SERS substrate for simultaneous determination of pesticides residue in tea via solid phase extraction coupled multivariate calibration. *LWT Food Science and Technology*, 105: 290-297.
52. Chen, C., Liang, X., Wang, J., Shaolei, Y., Yan, Z., Cai, Q. and Yao, S. (2013). Development of a highly robust solid phase microextraction fiber based on cross-linked methyl methacrylate-polyhedral oligomeric silsesquioxane hybrid polymeric coating. *Analytica Chimica Acta*, 792: 45-51.
53. Yang, L., Zhang, J., Zhao, F., and Zeng, B. (2016). Electrodeposition of self-assembled poly(3,4-ethylenedioxythiophene) @gold nanoparticles on stainless steel wires for the headspace solid-phase microextraction and gas chromatographic determination of several polycyclic aromatic hydrocarbons. *Journal of Chromatography A*, 1471: 80-86.
54. Yang, Y., Li, Y., Liu, H., Wang, X., & Du, X. (2014). Electrodeposition of gold nanoparticles onto an etched stainless steel wire followed by a self-assembled monolayer of octanedithiol as a fiber coating for selective solid-phase microextraction. *Journal of Chromatography A*, 1372: 25-33.
55. Xiao, C., Han, S., Wang, Z., Xing, J., Wu, C. (2001) Application of the polysilicone fullerene coating for solid-phase microextraction in the determination of semi-volatile compounds. *Journal of Chromatography A*, 927: 121-130.
56. Chen, J. M., Zou, J., B., J., Zeng, X. H., Song, J. J., Ji, Y. R., Wang, Chen, J. and Ha X., (2010) Preparation and evaluation of graphene-coated solid-phase microextraction fiber. *Analytica Chimica Acta*, 678: 44-49.
57. Zhang, Y., Yang, Y., Li, Y., Zhang, M., Wang, X. and Du, X. (2015). Growth of cedar-like Au nanoparticles coating on an etched stainless steel wire and its application for selective solid-phase microextraction. *Analytica Chimica Acta*, 876: 55-62.
58. Bian, W., Liu, Z., Lian, G., Wang, L., Wang, Q. and Zhan, J. (2017). High reliable and robust ultrathin-layer gold coating porous silver substrate via galvanic-free deposition for solid phase microextraction coupled with surface enhanced Raman spectroscopy. *Analytica Chimica Acta*, 994: 56-64.

59. Liu, H., Liu, L., Li, Y., Wang, X. and Du, X. (2014). Preparation of a robust and sensitive gold-coated fiber for solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental waters. *Analytical Letters*, 47(10): 1759-1771.
60. Liu, H.-X., Yang, Y.-X., Ma, M. G., Wang, X.-M. and Du, X.-Z. (2015). Self-assembled gold nanoparticles coating for solid-phase microextraction of ultraviolet filters in environmental water. *Chinese Journal Analytical Chemistry*, 43(2): 207-211.
61. Gutierrez-Serpa, A., Rocio-Bautista, P., Pino, V., Jimenez-Moreno, F. and Jimenez-Abizanda, A. I. (2017). Gold nanoparticles based solid-phase microextraction coatings for determining organochlorine pesticides in aqueous environmental samples. *Journal of Separation Science*, 40(9): 2009-2021.
62. Tran, Q. H., Nguyen, V. Q. and Le, A. T. (2013). Silver nanoparticles: synthesis, properties, toxicology, applications and perspectives. *Nanoscience and Nanotechnology*, 4: 033001.
63. Djerahov, L., Vasileva, P., Karadjova, I., Kurakalva, R. M. and Aradhi, K. K. (2016). Chitosan film loaded with silver nanoparticles-sorbent for solid phase extraction of Al(III), Cd(II), Cu(II), Co(II), Fe(III), Ni(II), Pb(II) and Zn(II). *Carbohydrate Polymer*, 147: 45-52.
64. Bagheri, H. and Banihashemi, S. (2015). Sol-gel-based silver nanoparticles-doped silica-polydiphenylamine nanocomposite for micro-solid-phase extraction. *Analytica Chimica Acta*, 886: 56-65.
65. Gao, Y., Xia, B., Liu, J., Ji, B., Ma, F., Ding, L., Li, B. and Zhou, Y. (2015). Development and characterization of a nanodendritic silver-based solid-phase extraction sorbent for selective enrichment of endocrine disrupting chemicals in water and milk samples. *Analytica Chimica Acta*, 900: 76-82.
66. Baysal, A., Kahraman, M. and Akman, S. (2009). The solid phase extraction of lead using silver nanoparticles – attached to silica gel prior to its determination by FAAS. *Current Analytical Chemistry*, 5: 352-357.
67. Gopidas, K. R., Whitesell, J. K. and Fox, M. A. (2003). Synthesis, characterization, and catalytic applications of a palladium-nanoparticle-cored dendrimer. *Nano Letters*, 3(12): 1757-1760.
68. Yang, Y., Guo, M., Zhang, Y., Song, W., Li, Y., Wang, X. and Du, X. (2015). Self-assembly of alkyldithiols on a novel dendritic silver nanostructure electrodeposited on a stainless steel wire as a fiber coating for solid-phase microextraction. *RSC Advances*, 5(88): 71859-71867.
69. Liu, C., Zhang, X., Li, L., Cui, J., Shi, Y. E., Wang, L. and Zhan, J. (2015). Silver nanoparticle aggregates on metal fibers for solid phase microextraction–surface enhanced Raman spectroscopy detection of polycyclic aromatic hydrocarbons. *Analyst*, 140(13): 4668-4675.
70. White, R. J., Luque, R., Budarin, V. L., Clark, J. H. and Macquarrie, D. J. (2009). Supported metal nanoparticles on porous materials. Methods and applications. *Chemical Society Reviews*, 38(2): 481-494.
71. Gutiérrez-Serpa, A., Napolitano-Tabares, P. I., Pino, V., Jiménez-Moreno, F., and Jiménez-Abizanda, A. I. (2018). Silver nanoparticles supported onto a stainless steel wire for direct-immersion solid-phase microextraction of polycyclic aromatic hydrocarbons prior to their determination by GC-FID. *Microchimica Acta*, 185(7): 341.
72. Jiang, N., Wang, J., Li, W., Xiao, J., Li, J., Lin, X., Xie, Z., You, L. and Zhang, Q. (2019). Silver nanoparticles-coated monolithic column for in-tube solid-phase microextraction of monounsaturated fatty acid methyl esters. *Journal of Chromatography A*, 1585: 19-26.
73. Yazdi, M. N., Yamini, Y. and Asiabi, H. (2018). Fabrication of polypyrrole-silver nanocomposite for hollow fiber solid phase microextraction followed by HPLC/UV analysis for determination of parabens in water and beverages samples. *Journal of Food Composition Analysis*, 74: 18-26.

74. Feng, J., Sun, M., Li, J., Liu, X. and Jiang, S. (2011). A novel silver-coated solid-phase microextraction metal fiber based on electroless plating technique. *Analytica Chimica Acta*, 701(2): 174-180.
75. Hasanli, F., Mohammadiazar, S., Bahmaei, M. and Sharif, A. A. M. (2018). Coating of sol–gel film on silver nanodendrite as a novel solid-phase microextraction fiber for determination of volatile aldehydes in edible oils. *Food Analytical Methods*, 11: 2149-2157.
76. Wang, L., Hou, X., Li, J., Liu, S. and Guo, Y. (2015). Graphene oxide decorated with silver nanoparticles as a coating on a stainless steel fiber for solid phase microextraction. *Journal of Separation Science*, 38(14): 2439-2446.
77. Liu, Z., Wang, L., Bian, W., Zhang, M. and Zhan, J. (2017). Porous silver coating fiber for rapidly screening organotin compounds by solid phase microextraction coupled with surface enhanced Raman spectroscopy. *RSC Advances*, 7(6): 3117-3124.
78. Qiu, L., Liu, Q., Zeng, X., Liu, Q., Hou, X., Tian, Y., and Wu, L. (2018). Sensitive detection of bisphenol A by coupling solid phase microextraction based on monolayer graphene-coated Ag nanoparticles on Si fibers to surface enhanced Raman spectroscopy. *Talanta*, 187: 13-18.
79. Forough, M., Farhadi, K., Molaei, R., Khalili, H., Shakeri, R., Zamani, A., and Matin, A. A. (2017). Capillary electrophoresis with online stacking in combination with AgNPs@ MCM-41 reinforced hollow fiber solid-liquid phase microextraction for quantitative analysis of Capecitabine and its main metabolite 5-Fluorouracil in plasma samples isolated from cancer patients. *Journal of Chromatography B*, 1040: 22-37.