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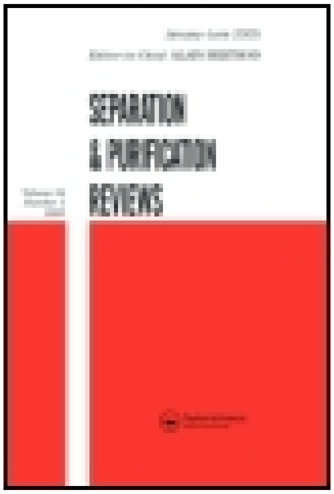

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Microextraction of Xenobiotics and Biomolecules from Different Matrices on Nano Structures

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Short running title: Nano structure for microextraction of biomaterials

MICROEXTRACTION OF XENOBIOTICS AND BIOMOLECULES FROM DIFFERENT MATRICES ON NANO STRUCTURES

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ABSTRACT:

Sample preparation is the backbone of any analytical procedure; it involves extraction and pre-concentration of the desired analytes; often at trace levels. The present article describes the applications of nanomaterials (carbon based inorganic and polymeric materials) in miniaturized extraction such as solid phase micro-extraction, stir-bar sorptive extraction, liquid phase micro-extraction, and dispersive liquid phase micro-extraction in the analyses of aqueous samples. The nanoparticles used for micro-extractions are discussed on the basis of their chemical natures. The synthetic route and the preparation of nanomaterials are described along with the optimization strategies for micro-extraction. A comparison between the conventional materials and nanomaterials for micro-extraction is proposed. The key roles of the nanomaterials for the micro-extraction of different analytes such as drugs, pesticides, polycyclic aromatic hydrocarbons, proteins and peptides from aqueous samples are reported. The use of nanomaterials, combined with miniaturized micro-extraction techniques, proved to be highly promising for sample preparation of various matrices with analytes at trace levels.

Keywords: Nanomaterials, micro-extraction, sample preparation, pesticides, drugs, environmental pollutants.

INTRODUCTION

Sample preparation is an integral part of the analyses as thousands impurities are present in different matrices. It is one of the most time consuming steps in the analyses of various analytes. It has been observed that about 60% analysis time is spent in sample preparation (1). In spite of this, sample preparation cannot be ignored during analyses. This implies that sample preparation is the bottleneck of analytical procedure, which involves the isolation and pre-concentration of the desired analytes from sample matrix (2). The conventional sample preparation methods i.e. liquid-liquid extraction (LLE), solid phase extraction (SPE), accelerated solvent extraction (ASE), microwave assisted solvent extraction (MASE) and matrix solid phase dispersion (MSPD) (3-7) usually involve large amount of sample volume, toxic solvents, multi-steps and time consumption (8). The use of toxic solvents increases the risk of environmental pollution and health hazards. Besides, the solvents are costly. Recently, novel miniaturized micro-extraction techniques were developed to overcome the limitations of conventional sample preparation methods (9). These new sample preparation techniques were highly welcomed as proved by the high number of publications on micro-extraction techniques and continuous increase (10).

Micro-extraction techniques, such as solid phase micro-extraction (SPME), stir-bar sorptive extraction (SBSE), liquid phase micro-extraction (LPME), micro solid-phase extraction (μ-SPE) and solid phase membrane tip extraction (SPMTE) have several advantages over the traditional approaches of liquid-liquid extraction (LLE) and conventional solid phase extraction (SPE) (11-18). The main advantages are minimal consumption of toxic solvents, less amount of sample needed and high enrichment factor obtained. All of these techniques are connected with analytical instruments either off-line, at-line or, sometimes, even on-line (19, 20).

Solid phase micro-extraction (SPME) is a promising sample preparation technique developed in 1990 (21, 22). It employs a chemically inert fused silica optical fiber or metal alloys fiber coated on the outside with a thin film of sorbent (23). Besides, thin film internally coated fused silica capillary column (8, 24), containing a polymeric organic compound acted as extraction phase. Most commonly used single coating and mixed coating fibers are polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), PDMS/DVB, DVB/PDMS/carboxen (CAR), carbowax (CW)/PDMS, CW/DVB, and CW/template resins. These coated fibers are usually utilized in two approaches during the extraction of analytes, either through headspace solid phase micro-extraction (HS-SPME) or direct immersion solid phase micro-extraction (DI-SPME) (8, 20, 25, 26). In spite of the crucial role of fibers, these have some limitations. Major drawbacks were lower thermal and chemical stabilities, high cost, low stabilities to non-polar organic solvents and less reusability, which devalue the applications of SPME technique (27-31). Stir bar sorptive extraction (SBSE) is also similar to SPME, involving a magnetic stir bar coated with same coated material as SPME fiber extracting phase. This modality shows high extraction capacity with less volume compared to what volume is needed with coated SPME fiber. Better enrichment factors are also obtained with SBSE compared to SPME. But the SBSE method normally suffers with long extraction and desorption time. The stir bar fiber cannot be directly injected into the split/split less injection port of GC instrument. Therefore, it is necessary to introduce a reconstitution step before proceeding to the chromatographic analysis (32, 33). Liquid phase micro-extraction (LPME) method commonly known as liquid-liquid micro-extraction (LLME) is a newly developed miniaturized technique for sample preparation of complex as well as trace level analytes. LPME has three different modes of extraction i.e. single drop micro-extraction (SDME), hollow fiber liquid phase micro-extraction (HF-LPME) and dispersive liquid-liquid micro-extraction (DLLME). Among these modalities, HF-LPME is most widely used robust and reliable method. In this method, the hollow fiber is most often made of polypropylene membrane. This form of HF-LPME method uses a donor phase (the sample solution), an acceptor phase (in the lumen of the hollow fiber) and the hollow fiber in between of these two phases. The pores of hollow fiber membrane are impregnated with organic solvent. The configuration of HF-LPME method can work with either two phase or three phases. In the two phase system, the aqueous sample solution acts as the donor phase while the organic solvent in the hollow fiber pores and lumen serves as acceptor phase. In the three phase system, both donor phase and acceptor phase are aqueous; and the hollow fiber is impregnated with organic solvent (34). HF-LPME and SDME are also convenient for the extraction of biomolecules from aqueous samples. But SDME is less robust than HF-LPME due to the instability of the droplet.

Nowadays, outstanding properties of nanomaterials continuously are attracting the scientists for the development of miniaturized micro-extraction techniques. Nanomaterials with sizes between 1 and 100 nm have unique thermal, mechanical, optical, electronic, magnetic and biological properties (35, 36). These can be easily exploited for miniaturized micro-extraction techniques (37-41). The surface properties (area, roughness, surface potential and electron distributions) of nanoparticles also enhance the interactions with matrices. The expected interactions such as hydrogen bonding, π-π stacking, dispersion forces, dative bonds, and hydrophobic interactions can affect the stabilities and selectivities of nanomaterials (42-45). Nanomaterials/ nanoparticles can be exploited on the basis of origin (natural, artificial), chemical nature (inorganic, organic, mixed), and homogeneity (single or hybrid composition). Nanoparticles are extensively discussed on the basis of chemical nature of analytes in many research as well as review articles (46-49). Nanoparticles of organic materials (carbon nanotubes, dendrimers and liposomes) and inorganic elements (metal oxides, semi-conductors, gold, silver, TiO_2, SiO_2, Fe_2O_3 etc.) are most widely used in extraction procedure (48). The use of nanoparticles as extraction probes for targeted analytes from sample matrixes (biological, environmental, food and spiked samples) is very interesting due to the following properties:

- Nanoparticles (NPs) are commercially available as well as easily synthesized and derivatized in laboratories. The properties can be modulated by controlling the syntheses variables, which can help for the selective interactions of target analytes (49).
- Most NPs have high porosity and surface area, which improve the extraction rate and efficiency (22, 50).
- Some NPs are biocompatible and useful for the extraction of biomolecules without any modification after interaction (49).
- Some NPs have special magnetic properties, simplifying the extraction procedure by using external magnetic fields (47).
- Other NPs have ionizing capabilities, helping direct analysis of sample by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) (47).

Consequently, the remarkable properties of nanoparticles are responsible for their applications in sample preparation. NPs have been used for micro extraction of various analytes such as pesticides, polycyclic aromatic hydrocarbons (PAHs), metal ions, or biomolecules in different matrices (environmental, biological, food and spiked samples). Therefore, the main objectives of this review are the applications of nanomaterials based micro-extraction techniques for the sample preparation of various drugs, pesticides, PAHs, metal ions and biomolecules in aqueous samples.

NANOMATERIALS FOR MICRO-EXTRACTION TECHNIQUES

Over the past two decades, the different types of nanomaterial are increasing rapidly. A variety of NPs with various shape (spheres, nanotubes, nanohorns and nanocages), different backbones (carbon, silica, silver, gold, semiconductors, TiO_2, SiO_2) have already been extensively review in various scientific fields such as analytical chemistry, material sciences, physics, medicine and electronics (51-53). We selected to focus on nanomaterials used as coating materials in SPME, components of the extracting phases in LPME and pseudo stationary phases in modern separation sciences for aqueous sample preparation (45, 54-59). The most commonly used nanomaterials based on chemical compositions/structures discussed in this work are shown in Figure 1.

Carbon Based Nanomaterials

Carbon exists in different allotropic forms with different structures and properties. In 1985, Kroto et al. (60) discovered a polyhedral nanostructure $C_{60,}$ fullerene. In fullerenes, the carbon atoms are bonded in arrangements of five to six membered rings. Fullerenes are apolar with aggregation tendencies facilitating their use as sorbents but their very low water solubility was a hindrance for use as coating on fibers. They can be used as sorbent materials after derivatization and/or polymerization. For instance, hydroxyfullerene have been used as SPME coatings (61). In 1991 Ijima et al. (62) discovered carbon nanotubes (CNTs) as tube like structure of graphene sheet, consisting of a single graphene sheet (single walled carbon nanotubes, SWCNTs) or a series of concentric layers (multiwalled carbon nanotubes, MWCNTs) (63). CNTs are the most exploited nanomaterials in the field of micro-extraction due to their remarkable properties such as:

- High thermal stability up to 1200 ºC, excellent mechanical and electrical properties, high tensile strength, good sorption capabilities and high surface area (64).
- CNTs show non-covalent interactions with analytes that include hydrogen bonding, π-π staking, dispersion forces, dipole-dipole interaction and hydrophobic effects (45).
- CNTs can be functionalized, derivatized and immobilized onto different materials (e.g. silica & steel). Functionalization includes carboxylic groups, which can be easily derivatized and immobilized. Immobilization of CNTs on inert glass or membranes reduces the aggregation tendency, resulting in higher surface area (65).

Moreover, the selectivity of extraction can be controlled by covalent or non-covalent functionalization on the surface of CNTs. The immobilization onto solid support helps to fabricate SPME device, which can be used as a coating material on SPME-fiber (66). For the excellent performance of extraction, MWCNTs are preferred oer SWCNTs as the presence of concentric sheets resulted in enhanced interactions with analytes (47).

Graphene (a parent form of fullerene), CNTs and graphite can extract analytes at the micro concentration level. Recently, some workers reported the applications of pristine or modified graphenes as highly efficient sorbents materials. These have been used for the extraction and removal of pollutants from aqueous solutions (67-69). The applications of graphene sheets for micro-extraction purposes received great attention due to some significant advantages such as;

- Graphene has a very large and highly conductive specific surface area for the fast adsorption equilibrium and analyte elution.
- Graphene can be easily synthesized from very common and inexpensive raw material (graphite). It does not require any catalyst suppressing contamination. Moreover it can be synthesized at very low cost (70).
- Graphene has plenty of sites for functionalization to manipulate the selectivity. It is easily functionalized as graphene oxide (GO). It is precursor of graphene in chemical synthesis and possesses many reactive groups (71).
- Graphene sheets are relatively soft and flexible. They can be attached onto a support more easily than CNTs or fullerenes. These graphene modified materials are very useful in preparing composite adsorbents and fabricating SPME devices (72).

Recently, the optically transparent, chemically inert and biologically compatible carbon nano-diamonds (CNDs) have been described as unique adsorbents for the extraction and determination of proteins, peptides and DNA (49, 73). Moreover, carbon-based nanomaterials also offer the possibilities of combining other types of nanomaterials to form nanocomposites. These are fullerene-Pd nanocrystals, poly (2, 5-dimethylaniline)-CNT, ceramic-CNT, teflon-CNT, and polypyrrole/graphene-composite. They all have been used for the extraction purpose (74-78). A wide variety of mesoporous carbons are also considered as extraction probes with significant improvement in micro-extractions.

Inorganic Nanomaterials

The applications of inorganic nanomaterials including silica nanoparticles, metal nanoparticles, magnetic nanoparticles are quite large. The quantum dots for micro-extraction of analytes also have remarkable efficiency. These dots have a good stabilities over a broad range of temperature, pH, they are not biodegradable, support long term administration and are easily functionalized. Moreover, several functional groups (from apolar saturated and unsaturated hydrocarbons to polar carboxylic acids, thiols, amines, and alcohols) can be introduced onto the surface of inorganic nanoparticles. Due to their unique properties, a wide range of inorganic NPs have been extensively used for sample preparation in separation science.

Silica NPs are highly appealing nanomaterials for micro-extraction due to several appreciable properties. The particle and pore sizes of silica can be changed from 50 nm to 300 nm and 2 nm to 10 nm, respectively with high stability, good surface area (> 700 m^2 g^{-1}), resistance to mechanical stress, degradation and different analytes loadings (79, 80). The internal as well as external surface of silica nanoparticles can be functionalized with different functional groups. Moreover, the different forms of silica NPs are easily synthesized in laboratories (81). Mesoporous silica materials (pore size 2 to 50 nm) are widely applied for micro-extraction. It is due to their easily functionalizable surface that can be rendered hydrophilic, hydrophobic, polar as well as positive or negatively charged, depending on bonded functional moieties. Up to now various forms of mesoporous silica materials such as mobile crystalline material (MCM) with MCM-41, MCM-48, Santa Barbara amorphous (SBA) such as SBA- 12, SBA-16, SBA-15, mesostructured cellular foam (MCF), hexagonal mesoporous silica (HMS), Fundan University silica such as FDU-12, and periodic mesoporous organosilica (PMO) were employed in sample preparation (82-89).

Metal nanoparticles (MNP) were discovered by Natan et al. (90-91). The immobilization of MNPs and metal-oxide on solid surfaces is quite cost effective, convenient and recyclable. Based on the previous review articles, ZnO, TiO_2, Al_2O_3, PbO_2, ZrO_2, MnO, CeO_2, gold nanoparticles (Au NPs), and silver nanoparticles (Ag NPs) were the most widely used MNPs for the extraction of organometallic traces organic compounds and proteins (92-105). Gold NPs have greater affinity towards thiol functional groups, which help for the extraction of amino-thiols (biomarkers of Alzheimer’s disease) through μ-SPE (106). Silver NPs have also been used as an extraction probe in LPME (49).

Magnetic NPs also have inherent properties for micro-extraction of analytes in biological matrices. Several types of iron oxides have been used as extraction probes in the micro-extraction. These include Fe_3O_4 (magnetite), α-Fe_2O_3 (hematite, weakly ferromagnetic or antiferromagnetic), γ-Fe_2O_3 (maghemite, ferrimagnetic), FeO (wüstite, antiferromagnetic), ε-Fe_2O_3 and β-Fe_2O_3. Among these magnetic NPs, Fe_3O_4 and Fe_2O_3 are most preferable and biocompatible candidates (107).

The quantum dots (QDs) are colloidal semi-conductive nanoparticles with very unique optical properties. Hence, these have good applications for the analyses of chemical and biological molecules. QDs such as CdS, PbS, ZnS, CuS and CdSe are used as extracting phases in LPME and specially for HS-SDME. These QDs allow for pre-concentration of volatile and semi-volatile compounds into a micro drop of extractant phase exposed to the headspace of the stirred sample solution (108). These quantum dots can have their surface modified for the interaction of biological entities. The advantages of QDs are integrated sampling, extraction, pre-concentration, and sample clean-up in a single stage. Moreover, non-volatile matrix interferences are reduced or eliminated (109-111).

Polymeric Nanomaterials

The advancements in the synthesis of nano-sized polymer as a sorbent materials boosted up the miniaturized micro-extraction techniques using conductive, non-conductive and molecularly imprinted polymers (MIPs). These nano-materials are used as a coating fibers and stationary phases in micro-extraction techniques. The conductive polymers are multifunctional, highly porous, extraordinary stable, and easily synthesizable with unique electrochemical properties (112-113). These properties made them convenient for SPME applications as coating fiber materials (114). Polyaniline (115-120), polypyrrole (121-124) and polythiophene (125-129) are the most popular conductive polymers used for the SPME fibers. However, their applications were limited due to low thermal stability, i.e. 200 ºC for polypyrrole and 220 ºC for polyaniline. But the use of protonated acids (inorganic and organic acids) has overcome this problem and made them stable at high temperature (up to 350ºC). Therefore, the derivatives of these polymers could also be used as significant polymeric materials for micro-extraction strategies (130, 131).

Some non-conductive polymers such as polyurethane, polycarbonate, polyamide and polyvinylchloride also were exploited for the formation of nano-fibers by applying the methodology of electro-spinning of polymers into nano-fibers. However, these "fabric like" nanostructured polymers have limitations especially due to their low thermal stability i.e. polyamide and polyurethane fibers have thermal stability up to 200°C and 225°C, respectively. Their large surface area and multi-functional capability made them convenient for SPME coatings (46).

Molecularly imprinted polymers (MIPs) are crossed linked co-polymers, synthesized in the presence of a template molecule. After copolymerization, the templates are removed, resulting into porous cavities with specific molecular size, shape and functionality inducing recognition properties for the template molecule. MIPs were developed and exploited as sorbent materials for micro-extraction purposes with a high selectivity, mechanical strength, and resistance against acids, bases, organic solvents and pressure and temperature. MIPs were also used as packing materials in capillaries in-tube SPME(s), which resulted in high enrichment factors, ease of automation and fast operation. Therefore, the preparation of silica fibers coated with MIPs is widely employed as a sorbent for miniaturized micro-extraction techniques (132, 133). However, this methodology has some drawbacks such as lack of compatibility between the solvents needed to adsorb and to desorb analytes from the MIPs. Thus, the use of several mobile phases and extra instrumentation are required.

Some inorganic NPs, i.e. alumina, silica, titanium dioxide and ferric oxy-hydroxides, have been used as substrates for the formation of new extraction materials with ionic surfactants coated on the surface. The external adsorbed ionic surfactants allow for the extraction of analytes from various sample matrices. On the basis of surfactants concentration, hemimicelles (low concentration of surfactants, hydrophobic), mixed hemimicelles and admicelles (high concentration of surfactants, hydrophilic) are formed. Hemimicelles are helpful for the extraction of a polar analytes in aqueous samples matrixes. Contrarily, admicelles help in extraction of apolar compounds. These types of surfactant coated NPs have been employed for the micro-extraction of biomolecules from different aqueous samples (47, 49). The applications of all NPs for SPME or LPME of various analytes from aqueous samples are summarized in Table 1.

SYNTHESES OF NANOPARTICLE-BASED MICROEXTRACION PROBES

Syntheses of nanomaterials are essential parts for micro-extraction as uptake of analytes depends on the interactions among analytes and adsorbents. These interactions can be monitored with the help of chemical reactions or chemical forces. Syntheses and coating techniques for most commonly used nanoparticles such as carbon nanotubes (CNTs), mesoporous silica and MIPs are reviewed in this section helping to understand interaction with analytes.

Syntheses of carbon nanotubes

CNTs can be synthesized by three different methods (i) catalytic arc discharge (CAD), (ii) laser ablation (LA) and (iii) chemical vapour deposition (CVD) (62, 134-136). Among these methods, CVD is the most promising method due to relatively low growth temperature, high yields and purities. Besides, the purifications of synthetic CNTs are important because of the presence of carbonaceous, metallic, fullerenes, amorphous carbon and others impurities. Some purification methods such as chemical oxidation, physical separation and combinations of chemical and physical techniques have been developed for obtaining CNTs with desired purities (137-140). After synthesis and purification of CNTs, chemical characterization is also performed with sophisticated techniques. Electronic microscopy is quite useful for the direct observation of impurities and the dimensional analyses of CNTs (141, 142). The evaluation of size, morphology and spatial orientation of CNTs can be performed with scanning electronic microscopy (SEM). Transmission electronic microscopy (TEM) is employed to measure the diameter and elucidate the numbers of walls and distance among them. A destructive thermo-gravimetric analysis (TGA) is helpful for the qualitative and quantitative determination of the metal impurities based on the thermal decomposition of the nanotubes (143, 144). However, TGA is not appropriate for quantitative measurement of carbonaceous residues because of other factors (i.e. defects on the wall surface), influencing the burning range of temperatures. Therefore, Raman spectroscopy is one of the most promising techniques for characterization and impurity evaluation of CNTs (145, 146).

The acidic character of CNTs, due to the presence of acidic oxygen and diverse oxygen containing groups, can be ascertained by Boehm titration using different bases of various strengths ($NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$) (147). The modifications and functionalizations on the surface of CNTs can also be confirmed with some other spectroscopic procedures such as nuclear magnetic resonance (NMR) (148) and fourier transform infrared spectroscopy (FT-IR) (149). The surface modifications (oxidation and functionalization) of CNTs made them convenient for the solubilities in organic and aqueous solvents. The oxidation of CNTs introduces hydroxyl, carbonyl and carboxyl groups. These result into bonded surface oxygen-containing radicals that have abilities to retain a variety of an extractants with appropriate pH. Oxidation of CNTs is carried out by refluxing in the presence of acidic medium such as nitric acid (HNO_3), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) or mixtures. Moreover, some oxidizing reagent, such as potassium permanganate ($KMnO_4$) or hydrogen peroxide (H_2O_2) may also be used for this purpose (150).

The functionalization of CNTs can be carried out by binding a series of functional groups to the side walls or termini of the tubes through different chemical reactions or physical interactions. The chemical functionalization of CNTs involves the covalent linkages among carbon atoms of CNTs and functional groups. These occur either by side walls (side wall functionalization) or through carboxylic groups and defects generated by oxidation (defects functionalization). Covalent side wall functionalization is carried out with a change of hybridization from sp^2 to sp^3. A simultaneous loss of π-conjugation system occurred on graphene layer in presence of highly reactive molecules such as fluorine. The details of chemical and physical functionalizations are extensively reviewed in various review articles (151, 152). Physical functionalization involves polymer wrapping, surfactant adsorption and endohedral method. These methods are based on non-covalent interactions such as van der Waal's forces, π-π stacking, physical adsorption and capillary effects between nanotube and functional molecule. These strategies are helpful to overcome the problems of chemical functionalization such as unwanted defects, electrical and thermal conductions of CNTs, respectively.

The synthesized or chemically treated (oxidation/functionalization) CNTs have been used as a coating materials for solid phase micro-extraction (SPME) technique. The applications of CNTs coated fibers are reviewed by Mehdinia et al. (46). The coatings of SWCNTs and MWCNTs onto the fibers play interesting role in the extraction of analyte at trace or low level. The SPME fibers can be prepared by using sol-gel technology (153-155), physical agglutinating method (156-160) and electrophoretic deposition (EPD) (161-164). Moreover, electrochemical polymerization was also reported for MWCNT-based SPME fibers (124, 165,166). Among these methods of coating, sol-gel method has good recognition due to the formation of strong chemical bonds between substrate and coating, solvent durability and good extraction efficiency.

Syntheses of silica and inorganic nanoparticle products

In the field of SPME, the applications of silica NPs (mesoporous silica, as fiber coating material) have better selectivities and adsorptions than the raw silica. Hou et al. (167, 168) reported mobile crystalline material MCM-41 and phenyl functionalized MCM-41 mesoporous organosilicas as fiber coatings in SPME. Synthesis of mesoporous silica materials may be performed with two different strategies i.e. using a liquid-crystal as a template through a cooperative self-assembly process (169). In this process, different types of surfactants (neutral block copolymer, cationic or anionic surfactants) were used with diverse additives (tri-methyl benzene, alcohols and salts) in the presence of acidic or basic media at different temperatures. Various mesoporous silica materials such as the already cited MCM-41 with two-dimensional hexagonal crystal (p6mm) (82), or SBA-12 with three-dimensional hexagonal crystal ($P6_3$/mmc) (170), or SBA-16 with three-dimensional cubic (Im3m) (171), lamellar (172), cellular foam (83) can be prepared with different pore sizes by using different types of surfactants, additives, reaction temperatures and medium (basic/acidic).

The details of the synthesis strategies of various types of non-silica inorganic based mesoporous materials including ZrO_2, TiO_2, HfO_2, Gr_2O_3, Au, Pd, carbon CMK-1 and CMK-3 also have been explained in many research papers (173-176). After synthesis, the characterization of mesoporous materials is carried out with the same techniques as explained above for morphology, qualitative and quantitative determination and functionalization of silica NPs. Moreover, the specific surface areas and porous structures of the samples can be determined by analysing the results of nitrogen sorption at 77 K in a Micromeritics apparatus. These are based on Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively (177). All these rapidly synthesized mesoporous materials have been employed as adsorbents in micro-extraction devices and formed SPME coated fibers with the help of the described coating methods all recently reviewed by Mehdinia et al. (46).

Li et al. (178) reviewed the syntheses, functionalizations and applications of magnetic nanomaterials including Fe_3O_4 (magnetite), α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite, ferrimagnetic), FeO (antiferromagnetic), ε-Fe_2O3, β-Fe_2O_3 etc. Pena-Pereira et al. (179) explain the immobilization techniques of metal and metal oxides including gold, platinum, titanium, zinc, and silver. They made them convenient for micro-extraction purposes.

Molecularly-imprinted polymers are synthesized by co-polymerization of monomers in the presence of template molecules. The preparation of MIPs is relatively economic and easily monitored in the laboratories due to which MIPs have high attention in the field of separation sciences in the recent decade (180). For the synthesis of MIPs, covalent, semi-covalent and non-covalent approaches have been proposed, depending on the bonding interactions between template and monomer (181-184). Among these approaches, non-covalent approach is most widely used because of the availability of different monomers and ease of interactions (hydrogen bonding, ionic interactions). First, MIPs were used for the packing of capillary employed in-tube SPME for the selective determination of propranolol in serum samples. These showed high enrichment factors and efficiencies (185). Keeping these points into consideration, Kosteret al. (186) used MIPs as coating materials for the formation of silica coated fibers used in SPME. Moreover, Sanagi et al. (187) synthesized MIPs and used as adsorbents in solid phase extraction (SPE) method. Various reports are available for micro-extraction of analytes using MIPs-SPME coated fibers and coating techniques for the preparation of micro-extraction probes (133, 180, 188, 189).

APPLICATIONS OF NANOPARTICLES IN AQUEOUS SAMPLES

As discussed above, the applications of nanoparticles have good recognition around the world for the micro-extraction of analytes present in complex samples or at trace level in aqueous conditions. Briefly, selected NP applications for the micro-extraction of various analytes from aqueous samples are presented.

Solid Phase Micro-Extractions

SPME techniques are most often combined with gas chromatography (GC), high performance liquid chromatography (HPLC) or capillary electrophoresis (CE) for the determination of the extracted analytes. When SPME is followed by GC analysis, the extracted analytes are thermally desorbed in the GC injection port. In case of HPLC, the extracted analytes get desorbed with different solvents from SPME coated fibers. Various reports of SPME coupled with CE are also available in the literature (190-192).

Lü et al. (159) employed stainless steel fibers coated with SWCNTs in SPME for the extraction of trace organochlorine pesticides in lake water and wastewater samples. The extraction efficiency was compared with commercial poly-dimethylsiloxane (PDMS) coating fibers. Rastkari et al. (156) performed micro-extraction of the ethers: methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME) from human urine samples (Figure 2). In this study, HS-SPME and SWCNTs were used followed by GC-MS analyses of extracted analytes. The extraction performances of the developed SWCNTs coated fibers were compared with commercially available PDMS fibers. It was confirmed that SWCNTs coated fibers had higher thermal stabilities, longer live spans (more than 150 cycles) and better sensitivities and precisions than commercial fibers. The developed method was also applied on the urine samples of 10 healthy male volunteers (Figure 2). The internal standard (IS) (1.0 μg mL^{-1}) was dioxane.

Wang et al. (66) used MWCNTs coated fused silica fibers in SPME coupled with GC-ECD for the determination of polybrominated diphenyl ethers (PBDEs) in water and milk samples. The results indicated that high enrichment factors (from 620 to 1800) were obtained compared to poly coating (5 % divinylbenzene - 95 % dimethylsiloxane) and activated carbon coatings with enrichment factors from 140 to 400 and 200 to 420, respectively. The developed method was applied for the extraction of PBDEs in local river water, waste water, and milk samples. The percentage recoveries were between 90% and 120% of PBDEs in 500 ngL^{-1} spiked samples.

Tang et al. (193) studied micro-extraction of bovine fibrinogen (BFg) and bovine serum albumin (BSA) proteins from complex proteins matrix. For this purpose, PDMS fibers coated with MWCNTs and SWCNTs were used as adsorbents in SPME procedure. These authors also confirmed that BSA was highly absorbed into the surface of SWCNTs as compare to MWCNTs. The results were opposite in the case of BFg because of the much larger size of the fibrinogen protein compared to the diameters of SWNTs.

Yazdi et al. (194) prepared poly(ethylene glycol) grafted-MWCNTs fibers using sol-gel technique. These were used as adsorbents in SPME for the extraction of benzene, toluene, ethylbenzene and *o*-xylene in water samples. The extracting analytes were determined by GC-

FID under optimal conditions. The optimizing parameters for the extraction efficiency of all analytes were studied. The relative standard deviations (RSDs) for one fiber (n = 5) and between fibers or batch to batch (n = 3) were in the range of 4.40-5.75% and 4.31-6.55%, respectively. The relative percentage recoveries for the spiked water samples at 20 pg mL^{-1} were in the range of 90% to 102%.

Recently, See et al. (18) used MWCNTs as adsorbents for the extraction of triazine herbicides from environmental water sample through a newly developed micro-extraction technique known as solid phase membrane tip extraction (SPMTE). The extracted analytes were analyzed by μ-HPLC. These authors also compared the SPMTE extraction procedure with reference method SPE-MIP and concluded that SPMTE was less time consuming, cost effective, easy to use, and highly reproducible using less solvent, still giving comparable LODs.

Basheer et al. (195) used MWCNTs for the extraction of organophosphorus pesticides: triethylphos-phorothioate, thionazin, sulfotep, phorate, disulfoton, methyl parathion, and ethyl parathion, from environmental samples using μ-SPE modalities and analyzed by GC-MS. The extraction performance of μ-SPE was also compared with the extraction performances of hollow fiber membrane-protected SPME (HFM-SPME) and headspace SPME (HS-SPME). The optimized conditions for higher extraction efficiency were achieved. The authors concluded that this method showed good linearity in the range of 0.1-50 μgL^{-1} with acceptable repeatability of the extractions (RSDs 2-8 %) for four sets of experiments. LODs were in the range of 1-7 pg g^{-1}. Each μ-SPE device could be used up to 30 extractions.

Jiménez-Soto et al. (196) carried out micro-extraction of triazine herbicides (terbutylazin desethyl, prometon, simazine, atrazine, propazin, terbumeton, secbumeton, desmetryn, simetryn, prometryn and terbutryn) in water samples using dispersive μ-SPE. The eluted analytes were analyzed by GC-MS under selected ion monitoring (SIM) mode. In this study, micro-extraction was performed with oxidized single-walled carbon nanohorns (o-SWNHs) as adsorbents. For maximum extraction, the different variables such as type of organic eluents (acetonitrile, ethyl acetate, hexane and methanol), concentration of o-SWNHs (0.1-0.5 g L^{-1}), volume of eluting solvent (0.1-1.0 mL) were optimized. It was concluded that 0.2 mL methanol as eluting solvent and 0.2 g L^{-1} of o-SWNHs as the concentration of adsorbent were the optimum conditions for herbicide micro-extraction.

Xu et al. (197) developed μ-SPE method for the extraction of the polycyclic aromatic hydrocarbons (PAHs): fluorene, phenanthrene, anthracene, fluoranthene and pyrene from soil samples. For this task, microwave assisted extraction (MAE) was coupled with μ-SPE. The extracted analytes were determined by GC-FID and compared with GC-MS. In these experiments, graphite fibers were used as sorbents materials for the extraction of PAHs in sediment samples. The results concluded that the best extractions of these compounds were obtained at 50ºC microwave heating for 20 minutes. 5 minute time was suitable for using acetonitrile as a desorption solvent. The limit of detection (LOD) of PAHs was found in the range of 2.2-3.6 ng g^{-1}. The linearity ranges were between 0.1 and 50 or 100 μg g^{-1} for GC-FID, while in case of direct GC-MS the LOD values ranged from 1.7 to 5.7 μg g^{-1} (197). The developed method was successfully applied for the extraction of PAHs in river and marine sediments, indicating feasibility for genuine environmental solid sample analysis.

Rao et al. (198) studied the syntheses and characterizations of phenyl-functionalized MCM-41, MCM-41-R and Phen-MCM-41-R mesoporous silica. The prepared mesoporous silica materials were applied as fiber coatings for the extraction of dibutylphthalate. The results indicated that the extraction efficiencies of Phen-MCM-41 and Phen-MCM-41-R coatings were about 3-6 times higher than of corresponding MCM-41 and MCM-41-R. It was because of high adsorption onto the hydrophobic surfaces of Phen-MCM-41and Phen-MCM-41.

Wang et al. (199) synthesized mesoporous silica (MCF-1) and phenyl modified mesoporous silica materials (Ph-MCF-1). The authors used them as fiber coating materials in SPME for the extraction of seven brominated flame retardants (BFRs), including tetrabromobisphenol A, tetrabromobisphenol S) and related compounds and analysed with HPLC. The performances of these mesoporous materials were measured as the extraction efficiencies. These were also compared with commercial fibers. The results in terms of peak height are shown in Figure 3. This figure clearly indicates that better extraction efficiencies of four home-made fibers (MCF-1A, Ph-MCF-1A, MCF-1B and Ph-MCF-1B) as compared to three commercial fibers: 100 μm PDMS (nonpolar coating), 85 μm PA (polar coating) and 65 μm PDMS/DVB (middle-polar coating). Linearity range was 5.0 to 1000 μg L^{-1} with correlation coefficients (r^2) ranging from 0.9993 to 0.9999. The LODs were 0.4-0.9 μg L^{-1} with from 1.2 to 5.1% as relative standard deviations (RSD %) for five sets of experiments. The repeatabilities of fiber-to-fiber and batch-to batch were 2.5-6.5 % and 3.2-6.7%, respectively. The percentage recoveries of the BFRs from aqueous samples were in the range of 86.5 to 103. 6%.

Zhu et al. (177) carried out the synthesis of vinyl-SBA-15 mesoporous organosilica and used it as a coating material for fibers in SPME. The prepared fibers were used for the extraction of nonpolar aromatic compounds (benzene, toluene, ethylbenzene, *o*-xylene) and polar compounds (phenols). The authors compared the extraction efficiencies of their original product with those of selected commercial polydimethylsiloxane (PDMS) fibers. They concluded that among the six different fibers studied: direct-coated SBA-15 (25.0 μm), direct-coated vinyl-SBA-15 fiber (25.0 μm), commercial PDMS fiber (30.0 and 100.0 μm), sol-gel-coated SBA-15 fiber (105.0 μm) and sol-gel-coated vinyl-SBA-15 fiber (105.0 μm), the SBA-15 and vinyl-SBA-15 fibers gave higher extraction efficiencies for the extraction of aromatic compounds. In the case of phenols, the direct coated vinyl-SBA-15 fiber showed better affinity. Finally, the results confirmed that low RSDs and LODs, wide linear ranges with good recoveries and new ordered mesoporous vinyl-SBA-15 coated fibers were good alternatives to the commercial fibers tested (177).

Mehdinia et al. (131) developed a headspace SPME method for the extraction of the fatty acids: myristic acid (C14:0), palmitic acid (C16:0), heptadecanoic acid (C17:0), stearic acid (C18:0) and eicosanoic acid (C20:0), from zooplanktons using nanosized conductive copolymers of aniline and m-amino benzoic acid coated fibers. The extracted compounds were analyzed by GC-MS. In this experiment, some important extraction parameters such as extraction temperature, extraction time, ionic strength, stirring rate and headspace volume were optimized. The results from these findings indicated satisfactory accuracy, linearity, precision, detection, extraction efficiency, repeatability, reproducibility and selectivity with the values of single fiber repeatability and fiber to fiber reproducibility <5.7 % and <10.2 %, respectively. The LODs were in the range of 0.01 (C14:0)-6 μg L^{-1} (C20:0). The recoveries of the extracted fatty acids were in the range of 83% (C16:0) to 115 % (C14:0). Moreover, the correlation coefficients (r^2) of the calibration curves ranged from 0.992 (C20:0) to 0.998 (C18:0) with 0.5 to 20 μg mL^{-1} linearity range.

Gao et al. (200) studied extraction of four organochlorine pesticides: hexachlorocyclohexane, dichlorodiphenyl dichloroethylene, dichlorodiphenyl dichloroethane and dichlorodiphenyl trichloroethane, in water samples using a HS-SPME process. In this mode of extraction, the authors developed a new coating fiber with of a novel nanostructured polyaniline ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate or BMIM PF_6) composite on steel wire. The extraction efficiency also had been compared with common polyaniline and PDMS coatings. The optimized parameters: desorption time, stirring speed, extraction time, ionic strength, and extraction temperature were also optimized. The authors concluded that the results with RSDs for single fiber repeatability ranged from 2.3% to 8.7 % (n=6). The RSDs for fiber to fiber reproducibility (n= 6) were 4.2%-12.1 %. The LODs were between 0.12 and 0.31 ng L^{-1} with correlation coefficients > 0.999. The developed method was applicable for the extraction of above cited pesticides in lake water, waste water and sewage treatment plant effluent with good recoveries (89 to 113 %).

Mehdinia et al. (201) also developed the extraction of phthalate esters: dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), and diethylhexyl phthalate (DEHP), in water samples using a thermally stable conductive polymer: the self-doped polythiophene (SPT) electrodeposited in presence of fluorinated organic acid as coating of SPME fibers. The extracted analytes were determined by GC-FID. The extraction procedures were optimized with a Taguchi orthogonal array design (OA) with an OA_{16} (4^5) matrix including extraction temperature, extraction time, salt concentration, stirring rate, and headspace volume. The developed method was successfully applied for drinking mineral waters, tap water and seawater samples for the analyses of the above cited esters. The satisfactory recoveries of 90-107% were obtained.

Bagheri et al. (202-203) carried out μ-SPE of some triazine herbicides from aqueous samples using conductive polymers as adsorbents. Various sorbents including aniline-ortho-phenylene diamine copolymer, newly synthesized polypyrrole, MWCNT, C_{18} and charcoal were studied as extracting phases with optimized conditions. The findings of these experiments clearly supported conductive polymers as good adsorbents in μ-SPE for triazine herbicides in aqueous samples. The sensitivity and reproducibility were high. The LODs values of optimized methods were in the range of 0.01-0.04 ng mL^{-1}. RSDs (%) at a concentration level of 0.1 ng mL^{-1} were in the range of 4.5 to 9.3 % for (n=5) sets of experiments.

In addition to polymeric coatings of adsorbents, some molecularly imprinted polymers (MIPs) were also developed and employed as the extracting adsorbents in the micro-extraction techniques. First of all, the applications of MIPs were studied by Koster et al. (186) for the extraction of brombuterol in urine samples. Moreover, the applications of MIPs for the extractions of drugs, pesticides and other organic, inorganic compounds in aqueous samples have been well reviewed (132, 188, 189).

Liu et al. (204) carried out the extraction of fluoroquinolones antibiotics (FQs) in aqueous samples using molecularly imprinted polypyrrole/multi-walled carbon nanotubes (MIPPy/MWCNTs) composite coating on platinum wire. In this experiment, SPME was performed with electrochemical potential. In this technique, a direct current potential was applied to MIPPy/MWCNTs/Pt fiber as working electrode in a standard three-electrode system. FQ ions suffered electrophoretic transfer to the coating surface and then entered into shape-complimentary cavities by some chemical forces such as hydrogen-bonding and ion-exchange interactions. Some extractions parameters namely applied potential, extraction time, solution pH, ionic strength and desorption solvent were optimized. The results showed good selectivities and higher extraction efficiencies for the extraction of FQs as compared to the traditional SPME. After the extraction, the desorbed antibiotics (FQs) were analyzed by HPLC. The LODs values were obtained in the range of 0.5-1.9 μg L^{-1}. The developed method was employed for the analyses of FQs in spiked urine and soil samples. The results showed good performance with the extraction recoveries in the range of 85.1-94.2 and 89.8-95.5 % for urine and soil samples, respectively.

Liquid Phase Micro-extractions (LPME)

Nanoparticles are also recognized as effective probes for hollow fiber liquid phase micro-extraction (HF-LPME), single drop micro-extraction (SDME) and dispersive liquid-liquid micro-extraction (DLLME). Generally, these techniques are coupled with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and MALDI time of flight mass spectrometer (MALDI-TOF-MS) for the determination of biomolecules such as proteins, peptides, biomarkers, nucleic acids, microorganisms, drugs and carbohydrates (205).

Wei et al. (206) used magnetic nanoparticle for micro-extraction of nicotine in urine sample through three phases hollow fiber liquid phase micro-extraction (TP-HF-LPME) with good linearity range from (0.05-50 mgL^{-1}), LOD (3.0 gL^{-1}) and RSD (< 3 %). The method was also applied for the extraction of nicotine from urine samples of active and passive smokers. The amounts detected were 5.39 mg L^{-1} and 2.08 mg L^{-1} nicotine respectively, with extraction recoveries 95-100 %.

Lee and Shi (207) performed micro-extraction of a series of polycyclic aromatic hydrocarbons (PAHs) from environmental samples through DLLME coupled with D-μ-SPE. In this study, the authors used magnetic NPs as extracting probes. 1-Octanol was used as an extractant in DLLME. The optimum conditions for the extraction of PAHs were 3200 rpm for 2 min and 1 min vortex in D-μ-SPE followed by desorption with acetonitrile. The results of this combined method indicated that good extraction efficiencies with high enrichment factors ranged from 110 to 186 fold. The LODs and LOQs were in the range of 11.7-61.4 pg mL^{-1} and 0.04-0.2 ng mL^{-1}, respectively. The linearity ranged from 0.5-50, 1-50, and 2-50 ng mL^{-1} for different PAHs.

Sudhir et al. (92) performed the extraction of Met-enkephalin (Met-enk, H-Tyr-Gly-Gly-Phe-Met-OH) and Leu-enkephalin (Leu-enk, H-Tyr-Gly-Gly-Phe-Leu-OH) peptides from aqueous and urine samples through SDME using gold (Au) nanoparticles in toluene as an extracting phase. The isoelectric point (pI) of peptides played a crucial role for the extraction. The extracted peptides were identified by atmospheric pressure matrix-assisted laser desorption/ionization mass spectrometry (AP-MALDI-MS). The results of these findings indicated that the signal intensity for the peptides was enhanced significantly in the mass spectrum obtained with SDME relative to the signal intensity observed without micro-extraction.

Shastri et al. (205) prepared multifunctional gold nanoparticles modified with (4-mercaptophenyliminomethyl)-2-methoxyphenol in toluene. These were employed as binary matrix nanoprobes for SDME of low abundance of proteins and peptides in MALDI-TOF-MS. The authors concluded that the binary matrix approach, consisting of Au NP-SDME droplets and organic matrix (CHCA or SA), is homogeneously mixed to form homogenous crystals. These had high sensitivity for the detection of peptides and proteins at low concentration (f mol) in

MALDI-MS. Moreover, these nanoparticles were also acting as multifunctional nanoprobes for ionization, enrichment, pre-concentration and desalting purposes for a variety of peptides and proteins. The extracted sample could be directly deposited onto MALDI target plates and directly detected by MALDI-MS without washing or elution steps. Thus, sample loss can be avoided.

Wu and Kailasa (208) carried out DLLME of hydrophobic proteins (valinomycin and gramicidin D) using oleic acid capped Mg $(OH)_2$ nanoparticles as hydrophobic probes. The extracted proteins were determined by MALDI-MS (Figure 4). The results with optimum conditions for the extraction indicated good linearity ranges from 10-400 nM and 0.1-2.0 μM for valinomycin and gramicidin D, respectively. The LODs values were 2.0 nM and 24 nM for valinomycin and gramicidin D, respectively. MALDI spectra of both proteins (Figure 4) clearly indicated good extraction efficiencies of OA-capped Mg $(OH)_2$ NPs as compared with the direct analysis from aqueous solution with 2,5-DHB as matrix. Optimization of extraction parameters are also an integral part of this review. The effect of various parameters on the extraction efficiency is discussed in the next section.

OPTIMIZATION OF MICRO-EXTRACTION METHODS

The optimization of micro-extraction methods for the extraction of various analytes in aqueous samples is also an important factor for obtaining good percentage of recovery, selectivity, sensitivity, efficiency, and enrichment factor. First of all, the selection of micro-extraction methods depend on complexity, nature of sample and the properties of interested analytes and a number of optimizing parameters. The optimization parameters are extraction mode, agitation method, sample volume, sample pH, ionic strength, water content, organic solvent content, extraction time, desorption time, and sample temperature. These parameters can be optimized by determining the peak area of the analyte in the case of HPLC, GC and GC-MS techniques. The signal intensity of the analytes can be optimized in case of MALDI, MALDI-MS and MALDI-TOF-MS techniques.

Extraction Temperature

Temperature is a crucial extraction parameter for the determination of analytes in aqueous sample. Theoretically, when the sample temperature is increased, analyte diffusion also increases; resulting into enhancing of extraction or rate of mass transfer onto the fiber coating (209). However, continuous increasing of sample temperature may lead to the diminishing of distribution constant between the sample matrix and fiber coating, resulting into less sensitivity of method and low recovery of the analyte at equilibrium (209). Therefore, a slight variation in temperature may change selectivity, sensitivity and reproducibility. Gao et al. (200) studied the effect of extraction temperature on the extraction efficiencies of organochlorine pesticides (OCPs) in aqueous samples as shown in Figure 5 (A). The authors used the range of temperature from 20-60ºC and it may be concluded that there was a significant difference in the extraction efficiencies between 30 ºC and 40 ºC ($p < 0.05$). But the extraction efficiencies at 40ºC and 50ºC had no significant difference ($p > 0.05$). Therefore, 40ºC was the optimum as the maximum extraction efficiencies of these pesticides were achieved. Bagheri et al. (203) investigated the effects of temperature on the extraction efficiencies of phenol and chlorophenols [Phenol (Ph), 2-

chlorophenol (2CP), 4-chlorophenol (4CP), 2,4-di-chlorophenol (24DCP) and 2,4,6-tri-chlorophenol (246TCP)], using polyamide based nanofibers in SPME. The authors concluded that low temperature, normally, resulted into maximum extraction. Mehdinia et al. (131) also performed the extraction of fatty acids [Myristic acid (C14:0), Palmitic acid (C16:0), Heptadecanoic acid (C17:0), Stearic acid (C18:0) and Eicosanoic acid (C20:0)] on the different temperatures ranging 20-80ºC through HS-SPME. Here, the high 80ºC temperature was found to be the optimum extraction temperature.

Ionic Strength

Ionic strength of the sample solution increases with the addition of soluble salt, resulting into decrease of the aqueous solubility of many organic compounds (salting-out effect). Thus, the solute distribution constants (K_{es}) increase with improved sensitivity (210). However, an increase in ionic strength of the sample solution improves the extraction efficiency of target analytes as well as that of interfering compounds. The amount of extracted analytes may differ from the actual amount depending on the nature of analyte and salt concentration. The most commonly used salts are sodium chloride (NaCl), disodium phosphate (Na_2HPO_4), di-potassium carbonate (K_2CO_3) and sodium dihydrogen phosphate (NaH_2PO_4) (211, 212). Mehdinia et al. (131) analyzed the influence of ionic strength on the extraction efficiency of fatty acids by adding NaCl from 0 to 30 % (w/v). The authors concluded that 15% (w/v) NaCl was the optimum ionic strength for the extraction of all these fatty acids. Gao et al. (200) also used NaCl from 0 to 30% (w/v) (Figure 5 B) to increase ionic strength of sample resulting into increase of the partial pressure of volatile chlorinated pesticides in HS-SPME improving analyte extraction. They confirmed that 30% (w/v) of NaCl was the optimum. Moreover, Bagheri et al. (203) also optimized ionic strength of phenol and chlorophenol samples by adding NaCl from 0-35% (w/v). The authors observed that 25% (w/v) of NaCl was the optimum amount for appreciable extraction efficiency; except 2,4,6-tri-chlorophenol due to its higher hydrophobic character.

Sample pH

The sample pH also affects the extraction efficiency. The extraction of weak acid and weak base analytes is pH sensitive. The sample pH can easily be adjusted by appropriate buffers according to pKa values of the analytes. In case of acid analytes, the extraction efficiency may be improved lowering the sample pH (213). Similarly, the extraction efficiency of basic analytes is enhanced by using high sample pH values. For the extraction of analytes having both acidic and basic functionalities, the pH of the sample solutions should be adjusted empirically. Sudhir et al. (92) used both acidic and basic (pH 2.0-11.0) conditions for the extraction of peptides in droplet of gold NPs in toluene through SDME. The spectra of these peptides at pH 3.0 and 9.0 clearly indicate that the extraction can be achieved into gold NPs in toluene at sample pH values above their isoelectric point (pI=5.4). Basheer et al. (195) carried out the extraction of organophosporous pesticides (OPPs) with different samples pH ranging from 2-12. The results concluded that the extraction efficiency continuously increased from pH 2.0 to 8.0 and slightly decreased at pH > 8. This might be due to the hydrolysis of OPPs in highly alkaline medium.

Extraction Time

Extraction time is also a substantial optimizing parameter because the mass transfer of an analyte is a time dependant process. The equilibrium is attained in a specific time period. It may be quite long for highly hydrophobic target analytes. Most of the micro-extraction techniques are equilibrium based extraction. Kailasa et al. (214) optimized the extraction time for achieving higher extraction efficiencies of peptide mixtures (valinomycin and gramicidin D) from aqueous solution by using NPs-LPME/MALDI-MS. The workers used different time intervals ranging from 0.3 to 2 hours and found that one hour was the optimum extraction time for proteins/peptides. Shrivas et al. (93) also studied the effect of time for the extraction of gramicidin in plasma and urine samples by NPs-LLME/AP-MALDI-MS method using 0.2 to 2.0 hours of extraction time with a 1.5 hour optimum extraction time. Gao et al. (200) observed the effect of time on the extraction efficiencies of organochlorine pesticides (Figure 5 C). Based on their results, there was a significant difference in extraction efficiencies between 30 and 40 min ($p < 0.05$) with no significant increase after 40 min ($p > 0.05$) extraction time. Therefore, 40 min was selected as the optimum extraction time for this particular study (200).

Agitation (Stirring Speed)

A certain level of agitation is required to achieve the rapid equilibrium among the analytes and extracting probe. The different agitation methods such as fast sample flow, rapid fiber movement, vial movement, stirring and sonication have been employed for the extraction. The efficiency of the agitation method improves the extraction ratio of the analyte. Therefore, the selection of agitation method and the optimization play a crucial role in the sample preparation/micro-extraction (20). Among these agitations method, stirring is the most commonly used method. Moreover, the agitation method also enhances the extraction efficiencies in non-equilibrium conditions. The equilibrium can be attained in case of toluene by increasing the rotational speed of magnetic stirrer (215). Sudhir et al. (92) optimized the agitation/stirring speed for higher extraction efficiencies of peptides in aqueous samples using SDME. Gao et al. (200) used the stirring method for the extraction of above cited organochlorine pesticides optimizing the stirring speed between 0 and 600 rpm. The best results were obtained at 600 rpm that was also the maximum possible speed, the magnet getting out of balance at higher rpm.

Desorption Temperature, Time, Desorption Solvents and Volume

The desorption of extracted analytes depends on the method used: it is different in liquid or gaseous phase. In case of gas chromatographic studies, thermal desorption is the best method. The partition coefficient of analyte between the extracting probe and the gaseous phase is temperature dependant. On the other hand, desorption time should be optimum to be quantitative and to avoid carry-over effect. Therefore, the highest temperature that would not damage the extraction probe should be used to minimize the desorption time. Bagheri et al. (203) used 150-250 ºC desorption temperature for a period of 1-10 min for the desorption of phenol and chlorophenols off polymeric nanofibers (N6-based nanofiber). Furthermore, the authors concluded that 200 ºC was the optimum temperature with 4 min desorption time. In case of liquid chromatographic determination of extracted analytes, the desorption process can be performed by manual SPME interface and off line desorption. These approaches allow the dynamic and static desorption of extraction probes into mobile phase or another suitable desorption solvent. Therefore, the optimization of desorption solvent and volume is necessary for high extraction efficiencies. The most commonly used desorption solvents are methanol, acetonitrile, dichloromethane, hexane and methanol-water or acetonitrile-water mixtures. Moreover, the selected desorption solvent must be compatible with the mobile phase conditions. The desorption solvent volume must also be optimized in such a way that the extracting probe, bar or fiber can be dipped completely in a small volume for high sensitivity and good efficiency (20).

The optimized parameters used by various scientists for the extraction of selected analytes are summarized in Table 1 and, on the basis of literature, Figure 6 proposes a method for micro-extraction optimization.

CONCLUSION AND FUTURE PERSPECTIVES

In summary, the involvement of nanomaterials in miniaturized micro-extraction techniques is promising for micro-extraction of various analytes present in complex aqueous matrices. Nanomaterials including carbon based, inorganic and polymeric materials have shown good extraction efficiencies of target analytes. The significant advantages of NPs overcome the limitations of conventional micro-extraction sorbents: lower thermal and chemical stabilities, lower stabilities to non-polar organic solvents, and less reusability.

NPs offer unique opportunities for designing different forms of extraction probes used in solid phase micro-extraction and liquid phase micro-extraction. Moreover, some classes of NPs play a dual role (as probe and matrix) in MALDI analysis of biological samples. The availability of NPs at low cost is the key aspect for getting good recognition in the field of micro-extraction techniques. The cost or prices of NPs depend on their nature (carbon based, inorganic or polymeric substrates), purity and size distribution. Some reports for the synthesis and preparation of NPs as extraction probes were quickly summarized in this article. In brief, the "home" syntheses, characterizations, functionalizations and derivatizations of extraction materials were often cost effective as compared to commercially available products.

A successful extraction always needs the full optimization of numerous parameters such as temperature, extraction time, sample pH, ionic strength, stirring speed, desorption time, desorption temperature and desorption solvents. This review demonstrated the potential of nanomaterials for extractions of various analytes from aqueous samples and the optimization of micro-extraction modalities. The continuous development of nanomaterials as microextraction probes should replace classical extraction materials in a near future. Moreover, the involvement of nanomaterials in sample preparation will boost up the commercial firms that will introduce these materials as microextraction probes in the market at large scale with high purity and low cost.

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Table 1. Microextraction of various classes of analytes in aqueous sample by using different nanoparticles and optimized extraction conditions (extraction temperature, ionic strength, sample pH, extraction time, stirring speed, desorption temperature and desorption time).

Analytes	Sample matrix	Conc.	Microextraction techniques	Nanoparticles (NPs)	Optimized Parameters							LOD	Ref.
					Ext. temp. (°C)	Ionic stren. (%)	Sample pH	Extr. time (min)	Stir. speed (rpm)	Deso. temp. (°C)	Deso. time (min.)		
Organophosporous pesticides (OPPs)	Sewage sludge	5 µg L^{-1}	µ-SPE	MWCNTs	60, 80	NaCl- 5 %	8	30	1000	220-250	30	1-7 pg g^{-1}	195
Atrazine, terbutryn & ametryn	Aqueous	0.1 ng mL^{-1}	µ-SPE	Ppy, PANI-OPD	30	NaCl- 5 %	6	40	-	-	5	0.01-0.4 ng mL^{-1}	202

Analytes	**Sample matrix**	**Conc.**	**Microextraction**	**Nanoparticles (NPs)**	**Optimized Parameters**							**LOD**	**Ref.**
Hexachlorocyolohexane, dichlorodiphenyldichloroethylene, dichlorodiphenyldichloroethane & dichlorodiphenyltrichloroethane	water	200 ng L^{-1}	HS-SPME	BMIM PF_6	40	NaCl-30 %	-	40	600	250	3	0.12-0.31 ng L^{-1}	200
Terbuthylazin desethyl, prometon, simazine, atrazine, propazin, terbumeton,	water	5 & 100 µg L^{-1}	D-µ-SPE	o-SWNHs	-	-	6.9	2	1600	-	-	50-300 ng L^{-1}	196

Analytes	**Sample matrix**	**Conc.**	**Microextraction**	**Nanoparticles (NPs)**	**Optimized Parameters**							**LOD**	**Ref.**
secbumeton, desmetryn, simetryn, prometryn & terbutryn													
p-xylene & anthracene	water	1x10^{-6} mol L^{-1}	SPME	MCM-41	20	-	-	30	1000	-	3	6.9-20 nM	168
Benzene, toluene, ethyl-benzene & o-	water	20 pg mL^{-1}	HF-SPME	PEG-g-MWCNTs	30	NaCl-6 %	-	30	1000	250	20 s	0.6 - 3 pg mL^{-1}	194

Analytes	Sample matrix	Conc.	Microextraction	Nanoparticles (NPs)	Optimized Parameters							LOD	Ref.
xylene													
Benzene, toluene, ethyl-benzene, o-xylene (BTEX) & Phenols	water	100 μg L^{-1} for phenols & 10 μg L^{-1} for BTEX	SPME	Vinyl-SBA-15 mesoporous organosilica	25	-	-	30	1500	250	-	0.001-1.32 μg L^{-1}	177
Phenol (Ph), 2-chlorophenol (2CP), 4-chlorophenol	Aqueous	100 ng mL^{-1}	HS-SPME	nylon 6, nano fiber	30	Nacl-25%	-	40		200	4	2-10 ng L^{-1}	203

Analytes	**Sample matrix**	**Conc.**	**Microextraction**	**Nanoparticles (NPs)**	**Optimized Parameters**							**LOD**	**Ref.**
(4CP), 2,4-di-chlorophenol (24DCP) & 2,4,6-tri-chlorophenol (246TCP)													
Polybrominated diphenyl ethers	water & milk	500 ng L^{-1}	SPME	MWCNTs	-	-	-	30	1200	295	2	3.6-8.6 ng L^{-1}	66
Benzo[a]pyrene	water	2x10-8 mol L^{-1}	SPME	Phenyl-MCM-41	20	-	-	30	600	-	5	0.11 nM	216
Dimethyl phthalate (DMP), diethyl	water	50 ng	HS-SPME	Self-doped polythioph	80	NaCl-	-	60	800	300	2		201

Analytes	Sample matrix	Conc.	Microextraction	Nanoparticles (NPs)	Optimized Parameters							LOD	Ref.
phthalate (DEP), dibutyl, phthalate (DBP), & diethylhexyl phthalate (DEHP)		mL^{-1}		ene (SPT)		15%						0.08-0.12 ng mL^{-1}	
1,4-dioxane	water	50 ng mL^{-1}	HS-SPME	Self-doped polyaniline (SPAN)	40	NaCl-15%	6.5	3	200	250	2	0.1 ng mL^{-1}	130
Volatile Compounds (Hg(II), H2S, MMT, Se(IV) &	water	-	HS-SDME	CdSe/ZnS quantum dots (QDs)	-	Nacl-15%	-	1.5-4	-	-	-	1.6-9.4 µM	109

Analytes	Sample matrix	Conc.	Microextraction	Nanoparticles (NPs)	Optimized Parameters								LOD	Ref.
CH_3Hg^+														
Methyl tert-butyl ether (MTBE), ethyl tert-butyl ether(ETBE) & tert-amyl methyl ether (TAME)	Urine	50-1500 ng L^{-1}	SPME	SWCNTs	55	Nacl-1.5M	-	30	-	230	3		10 ng L^{-1}	156
Tetrabromobisphenol A,tetrabromobisphenol S & related compounds	water	50 µg L^{-1}	SPME	MCF-1 & Ph-MCF-1	30	-	-	30	1000	-	2		0.4-0.9 µg L^{-1}	199

Analytes	**Sample matrix**	**Conc.**	**Microextraction**	**Nanoparticles (NPs)**	**Optimized Parameters**							**LOD**	**Ref.**
Bovine serum albumin (BSA) & bovine fibrinogen (BFg)	phosphate buffer	0.5 mg mL^{-1}	SPME	MWCNTs & SWCNTs	-	-	5, 5.5	120, 150	-	-	60, 120	0.078 mg mL^{-1}	193
Gramicidin	Urine & plasma	0.53 µM	LLME	Modified Ag	25	NaCl-7%	7	90	900	-	-	0.13-0.16 µM	93
Valinomycin & Gramicidin D	Urine & plasma	0.40 & 0.80 µM	LPME	Ag_2Se	25	NaCl-3%	7	60	900	-	-	20-68 & 100-180 nM	214

Figure 1: Structure of carbon based nanomaterials, inorganic nanomaterials and polymeric nanomaterials. SWCNT: single wall carbon nanotube; MWCNT: multi-wall carbon nanotube.

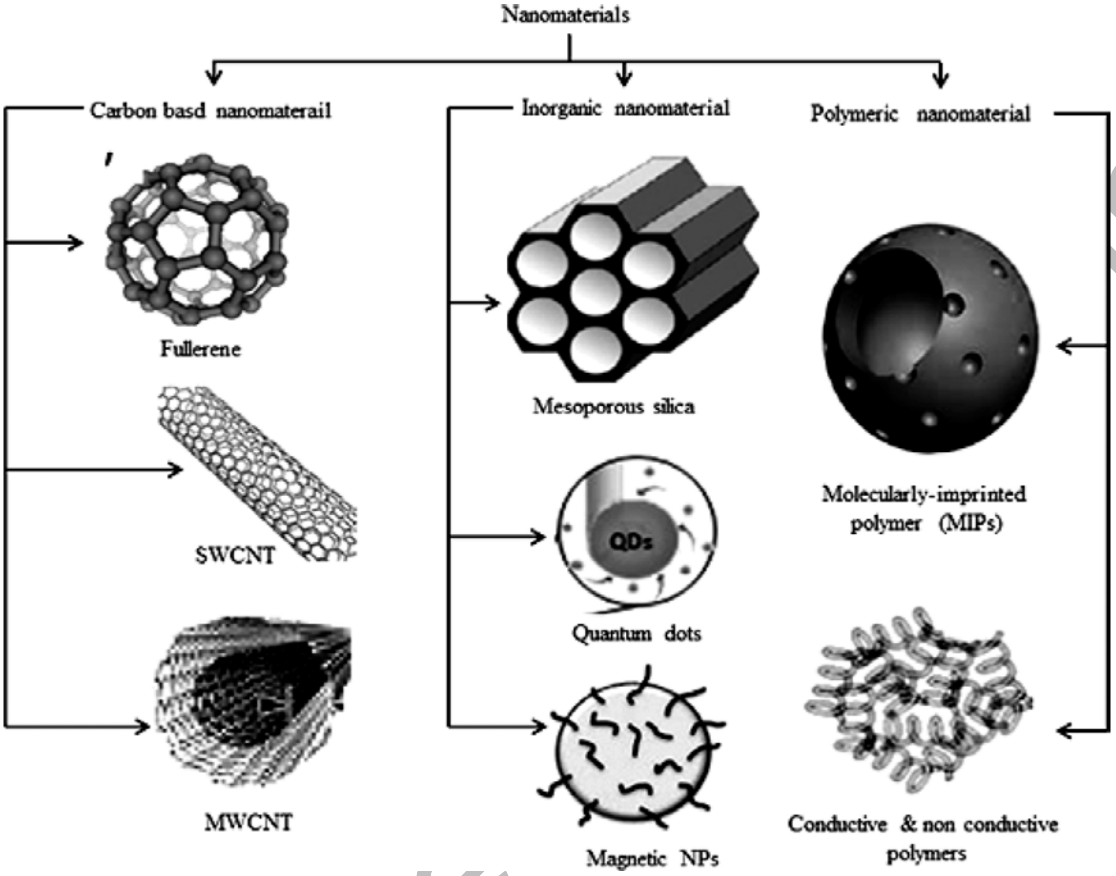


Figure 2: GC-MS chromatogram of extracted ethers from urine sample through solid phase micro-extraction (HS-SPME) by using SWCNTs coated fibers, (a) spiked control sample; (b) volunteer's urine sample, MTBE: methyl-t-butyl ether; ETBE: ethyl-t-butyl ether; TAME: t-amyl-methyl ether [156].

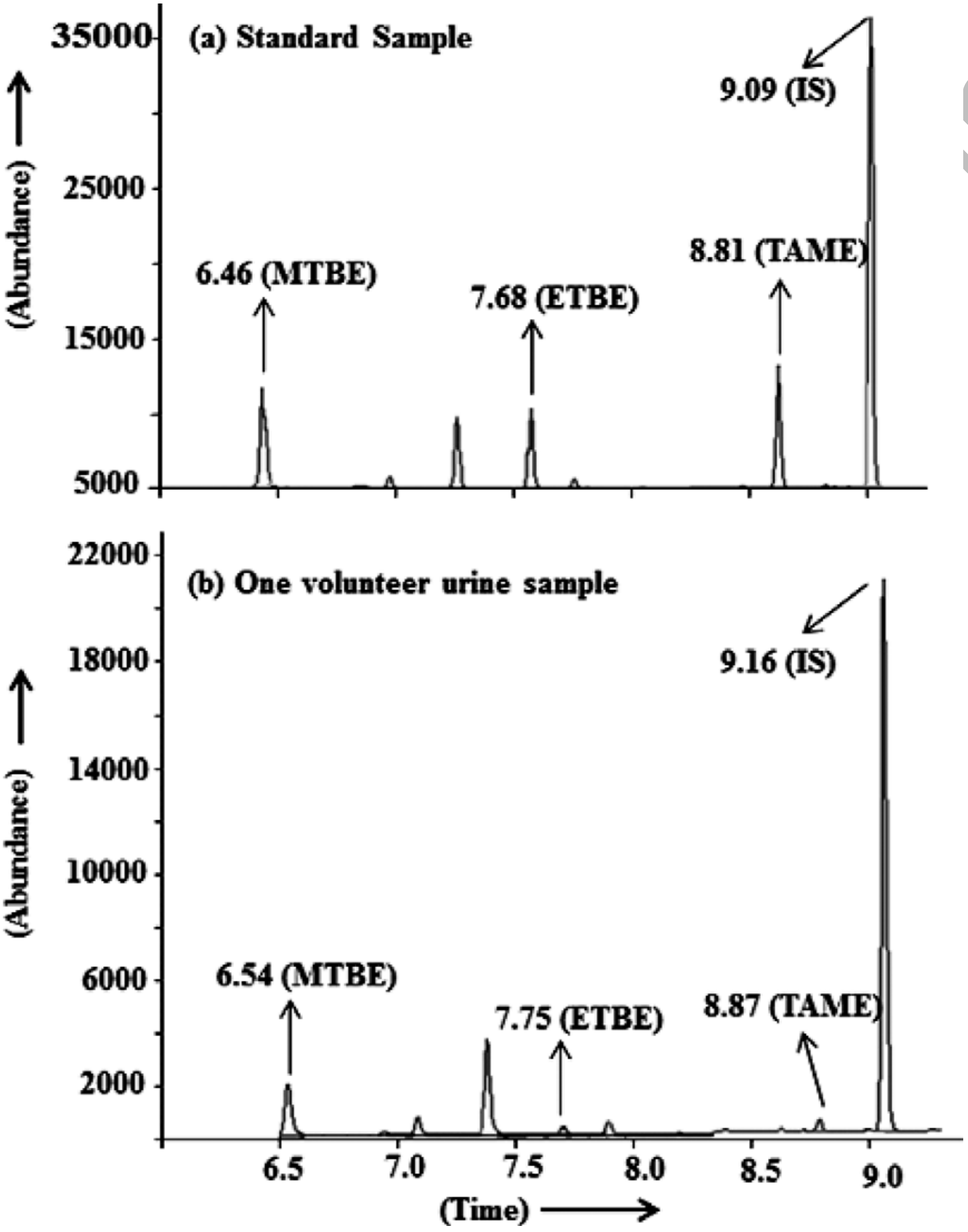


Figure 3: A comparison between synthesized mesoporous fibers and commercial fibers for the micro-extraction efficiency of brominated flame retardants (BFRs) tetrabromobisphenol (TBBP) A or S and bisphenol A (BPA) [199].

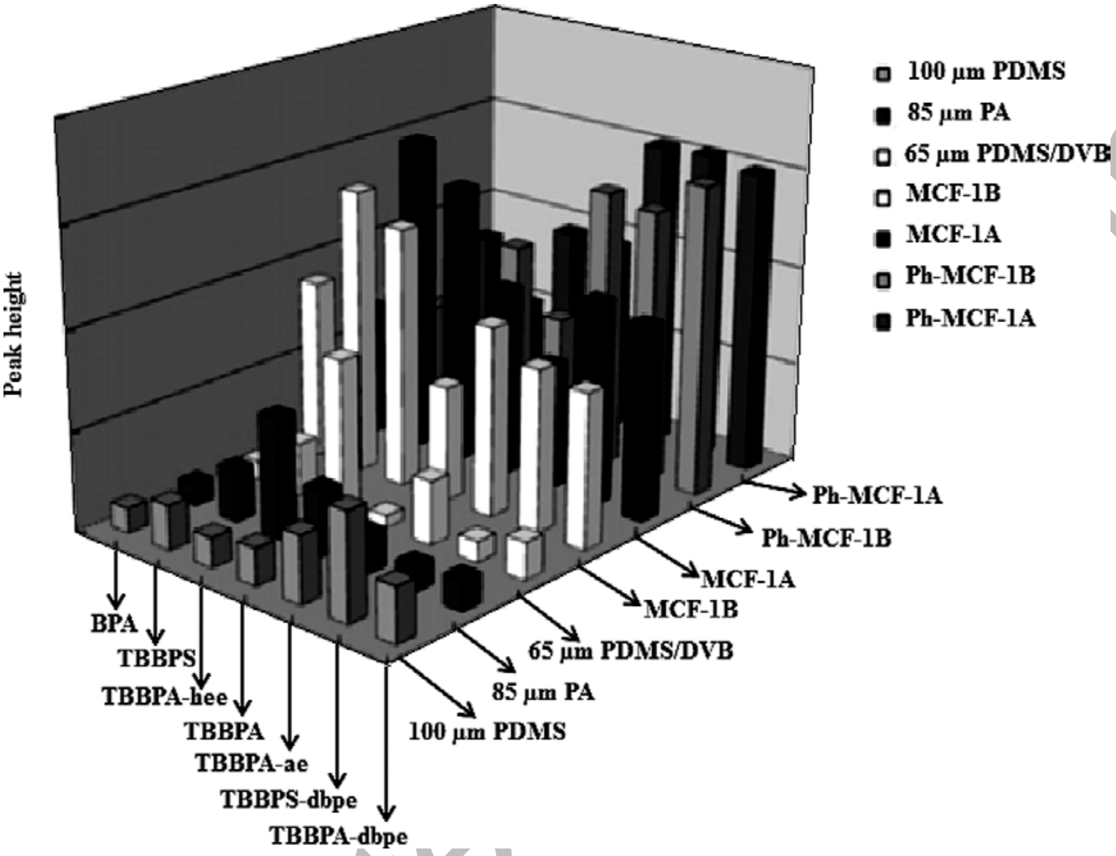


Figure 4: A MALDI comparison between (a) direct analysis from aqueous solution with 2,5-HB as the matrix and (b) OA-capped $Mg(OH)_2$ NPs-assisted liquid-liquid micro-extraction with 2,5-DHB for valinomycin (0.40 mM) and gramicidin D (2.0 mM) [208].

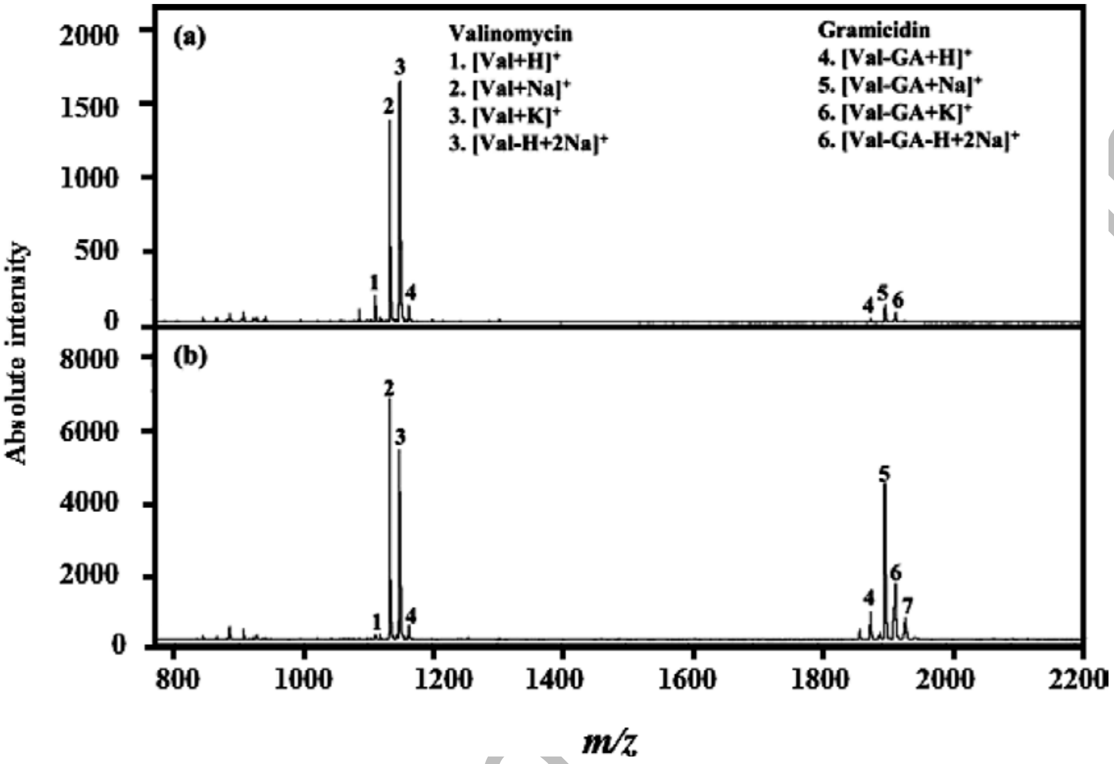
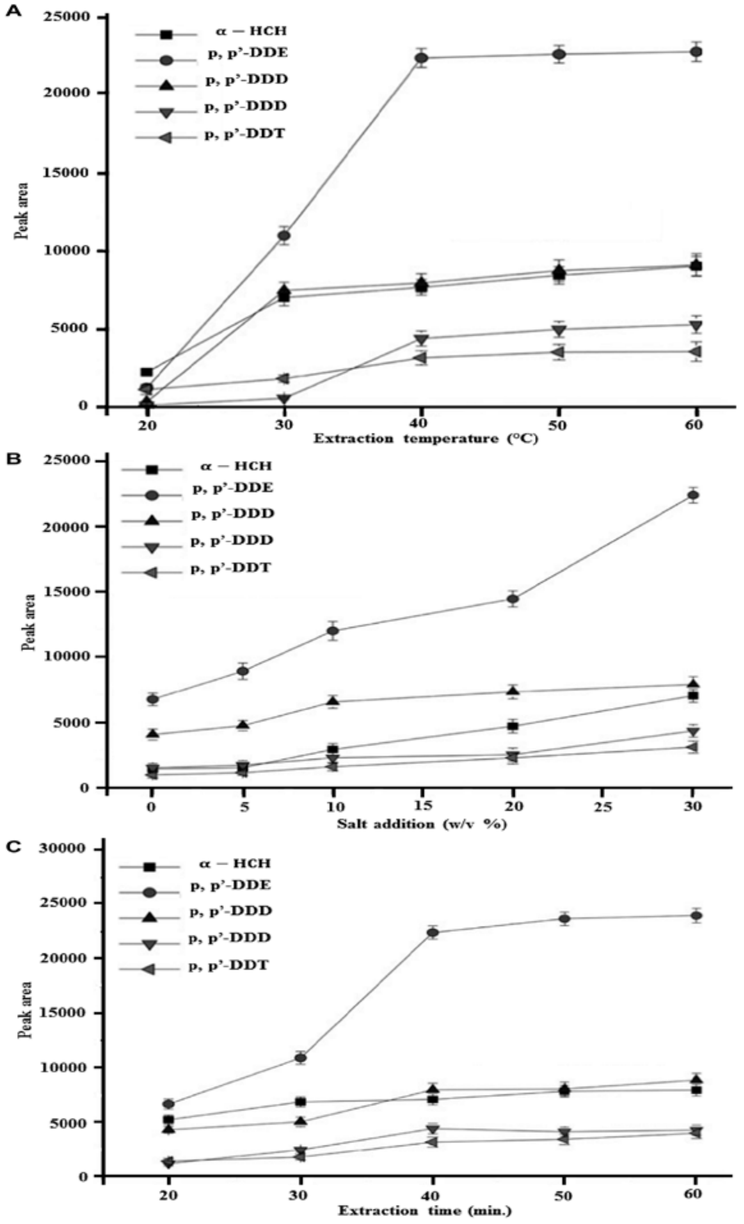


Figure 5: Effect of (A) extraction temperature, (B) addition of salt (ionic strength) and (C) extraction time on extraction efficiency of the organochlorine pesticides: hexachlorocyclohexane (α-HCH), dichlorodiphenyl dichloroethylene (p,p’-DDE), dichlorodiphenyl dichloroethane (p,p’-DDD, o,p’DDD), dichlorodiphenyl trichloroethane (p,p’-DDT)] determined by GC [200].



HCH), dichlorodiphenyl dichloroethylene (p,p’-DDE), c

Figure 6: Schematic diagram for the selection of optimizing parameters for micro-extraction of analytes through different micro-extraction techniques.