Use of nanomaterials in sample preparation

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The article presents recent applications of nanomaterials (metallic, silica and carbon-based) in sample-preparation procedures for sample clean-up and preconcentration of the analytes. Solid-phase extraction, microextraction and filtration techniques reported in 2010-11 are presented and discussed.

Keywords: Clean-up; Dispersive solid-phase extraction (dSPE); Filtration; Magnetic nanoparticle (MNP); Microextraction; Nanomaterial; Preconcentration; Sample preparation; Solid-phase extraction (SPE); Solid-phase microextraction (SPME)

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1. Introduction

There has been unprecedented growth in analytical measurement techniques in the past few decades. Instrumentation (e.g., chromatography, spectroscopy and microscopy, and sensors and microdevices) has undergone phenomenal development. However, even with such modern, powerful instrumental techniques, the direct analysis of environmental and biological samples is not always possible due to low concentration of the analytes and matrix interferences. More often, one or more pretreatment steps are necessary with the goal of enrichment, clean-up and signal enhancement. Because sample preparation still consumes most time and labor in the analytical procedure, attempts are made to improve this step in terms of speed, reliability and sensitivity.

Nanomaterials, with physical features less than 100 nm in one or more dimensions, have attracted great attention from scientists in recent years, mainly due to their unique, attractive, thermal, mechanical, electronic and biological properties [1]. Their high surface-to-volume ratio, the possibility of surface functionalization and favorable thermal features provide the flexibility needed in a broad range of analytical applications [2–5]. The nanosized structures may be in the form of particles, pores, wires or tubes. The physicochemical properties of nanomaterials can be controlled through structural design, incorporation of suitable components or modification of their surfaces.

An extensive review covering chemical and structural characterization of various nanostructured materials was published recently [6].

The aim of this article is to present the recent application of nanomaterials in sample-preparation procedures for sample clean-up and preconcentration of the analytes, which allows simplification of the method and the possibility of treating small amounts of sample. The solid-phase extraction (SPE), microextraction and filtration techniques reported during 2010–2011 period are presented. Some developments published in 2012 are also included. Interested readers could find more details regarding earlier contributions in reviews [7–10].

2. Nanomaterials

Generally, there are different approaches to classification of nanomaterials. The spectrum ranges over inorganic or organic, crystalline or amorphous particles, which can be found as single particles, aggregates, or powders or dispersed in a matrix. One way to use nanomaterials in sample-preparation protocols is to immobilize them on a solid support, particularly with magnetic properties [e.g., magnetite (Fe_3O_4) and/or maghemite (γ-Fe_2O_3)]. These hybrid nanomaterials can be easily separated from the dispersion with the aid

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of an external magnetic field. Also, the protective coating of nanomaterials stabilizes the magnetic shell and can be used for further functionalization to obtain multifunctional magnetic nanomaterials [3,11]. In particular, silanol groups on the silica coating provide many possibilities for surface functionalization.

For this article, the most used nanomaterials were organized into three types: metallic, silica and carbon-based. Examples of their application in sample-preparation procedures are discussed. In the second part, different formats of the applied nanomaterials are presented.

2.1. Metallic nanomaterials

The strong affinity that exists between gold nanoparticles (AuNPs) and polycyclic aromatic hydrocarbons (PAHs) has been used for extraction and preconcentration of these compounds from drinking water [12]. To extract pollutants, 500 μL of sample is mixed with 950 μL of solution containing AuNPs (20 nm of diameter). The mixture is then centrifuged for 20 min, supernatant is discharged, and the adsorbed analytes are eluted using 2 μL of 1-pentanethiol in 48 μL of *n*-octane. The entire extraction procedure consumes a very small volume of organic solvents per sample, which makes it environmentally friendly and relatively inexpensive.

Poly(ethylene glycol methacrylate phosphate (PEGMP) was proposed for the preparation of silver NPs (AgNPs) embedded polymer [13]. AgNPs were formed in the PEGMP matrix to impart bio-resistivity in the composite sorbent due to their antibacterial properties. This sorbent was applied for preconcentration of uranium from seawater and an active waste stream.

Nano-structured gold surfaces exhibit high affinity for dissolved mercury species [e.g., Hg(II) and $MeHg^+$] [14]. The Hg species trapped on the active gold collector can then be released as Hg^o vapor after thermal desorption at 550°C and measured by atomic fluorescence spectrometry with the limit of detection of 101–144 pg/L. The proposed procedure offers significant advantages over existing methods because no reagents are needed for sample preparation.

The adsorbent prepared by chemical reduction of Au(III) with hydroxylamine in the presence of suspended silica particles was also highly efficient for separation and enrichment of different mercury species from acidified water [15]. In addition, *in situ* preconcentration can easily be performed with a portable flow-injection system, thereby avoiding the need for stable reagents for sample transport and storage.

Nanosized metal oxides have unique properties (e.g., large specific surface area, high adsorption capacity and easy modification). Their adsorption strongly depends on morphology, crystal structure, defects, surface area and hydroxyl coverage. Several researchers used iron-oxide nanomaterials to enrich toxic ions [16–19] and organic pollutants from complex environmental matrices [20,21]. Homogeneous distribution of dispersed superparamagnetic NPs (e.g., Fe_3O_4, in solution) causes favorable mass transport to surfaces and can permit magnetic capture of depleted material. The adsorption of ionic surfactants onto the surface of iron-oxide NPs to form aggregates has been studied extensively [16,17]. These aggregates consist of monolayers (hemicelles) of surfactants adsorbing head down on the oppositely-charged metal-oxide surface and surfactant bilayers (admicelles) formed by hydrophobic chain-chain interactions of surfactants. The outer surface of hemicelles is hydrophobic, while that of admicelles is ionic, which provides two different mechanisms (hydrophobic and electrostatic interactions) for retention of target compounds. The number of commercially-available surfactants is enormous, hence the degree of hydrophobicity and the charge of the sorbent can be easily modified according to the nature of analytes. The physical or chemical modification of a sorbent surface was also proposed using 1-(2-pyridylazo)-2-naphtol [18], 1-hexadecyl-3-methylimidazolium bromide [21] and even tea waste from agriculture biomass [19] to improve the efficiency and the selectivity of the preconcentration processes.

Alumina-coated iron-oxide NPs modified with mixed hemicelles have been used for extraction and preconcentration of trace levels of cobalt [22]. Immobilization of 11-mercaptoundecanoic acid, yeast (*Yamadazyma spartinae*) and 4-aminophenylarsonic acid on TiO_2 NPs has been reported and used to preconcentrate toxic metal ions [23–25]. It was shown that, compared to nm-sized TiO_2 powder, this metal oxide in the form of a colloid has stronger adsorption ability for Cu(II), a higher adsorption rate and is more dispersive without agglomeration, giving a higher adsorptive repeatability [26]. With slurry sampling, the elution step could be omitted, so sample contamination and loss of analyte are avoided.

2.2. Silica nanomaterials

Silica is a very appealing material for analytical applications because it is relatively inexpensive, chemically inert and thermally stable. The silanol groups on the surfaces of silica NPs can be functionalized easily by treatment with the appropriate silane component [27]. Silica-coated magnetic NPs (MNPs) present the advantages of silica NPs with regard to surface reactivity and magnetic core, which contribute to the rapid separation of the sorbent carrying the target analytes from matrix solution. These NPs modified with mixed hemimicelles and chelating agents have been used for SPE of perfluorinated organic pollutants [28], bioactive herbal compounds from biological samples [29] and trace amounts of metals from various waters [30].

The combination of nanomaterials used as solid supports and supramolecular concepts has led to the development of hybrid materials with improved functionalities. Mesoporous silica nanomaterials have