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Silica-coated magnetic nanoparticles modified with γ-mercaptopropyltrimethoxysilane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry

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Abstract

We report here the synthesis of a new sorbent comprising silica-coated magnetic nanoparticles (SCMNPs) modified with γ-mercaptopropyltrimethoxysilane (γ-MPTMS) for solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb from biological and environmental samples. The prepared nanoparticles were characterized by infrared spectroscopy, transmission electron microscopy, and static adsorption-desorption experiments. These magnetic nanoparticles carrying the target metals could be easily separated from the aqueous solution simply by applying an external magnetic field; no filtration or centrifugation was necessary. Using this novel magnetic material, we have developed an efficient and cost-effective two-step method for detecting trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples. The first step of the method is a separation/preconcentration step, in which metals are adsorbed onto γ-MPTMS-SCMNPs. In the second step, inductively coupled plasma mass spectrometry is used to study the adsorbed metals. The effects of pH, sample volume, eluent, and interfering ions have been investigated. Under the optimized conditions, the limits of detection for Cd, Cu, Hg, and Pb were as low as 24, 92, 107, and 56 pg L^{-1}, respectively. Relative standard deviations (RSDs, $C=2$ ng L^{-1}, $n=7$) were 6.7%, 9.6%, 8.3%, and 3.7%, respectively.The proposed method has been validated using three certified reference materials, and it has been applied successfully in the determination of trace metals in biological and environmental samples.

Keywords: Magnetic nanoparticles; Heavy metal; γ-Mercaptopropyltrimethoxysilane (γ-MPTMS); Solid phase extraction; ICP-MS

1. Introduction

Heavy metal ion contamination represents a significant threat to the ecosystem and to fauna and flora. High concentrations may have severe toxicological effects on living organisms [1]. Considerable amounts of heavy metals enter the environment from metallurgy industries, combustion of coal, and automobiles. Heavy metals can easily enter the food chain through a number of pathways, and long-term exposure in a contaminated environment can cause progressive toxic effects due to gradual accumulation in living organisms over their life span [2]. Consequently, the development of reliable methods for the removal and determination of heavy metals in environmental and biological samples is of particular significance.

However, the direct determination of these elements in real samples is a difficult task. The main restrictions come from the complexity of the matrix and the extremely low concentrations of

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analytes in those samples, which are often below the detection limits of available techniques. Thus, highly sensitive and selective techniques are required. Inductively coupled plasma mass spectrometry (ICP-MS) is considered a powerful technique for trace and ultra-trace elemental analysis because of its very low detection limits for most elements. However, it is not free of interference effects, specifically spectroscopic interference and matrix effects [3,4]. The first type of interference arises as a result of isobaric overlap, polyatomic or adduct ions, refractory oxide ions, and doubly charged ions. This type of interference can be corrected with arithmetic algorithms. The second type of interference is more complex and is related to the nature of the sample matrix. The isotopes of interest and their most severe polyatomic ion interferences are summarized in Table 1. Spectroscopic interference in ICP-MS can be minimized using high-resolution (HR) ICP-MS [3] and collision/reaction cell ICP-MS [4]. However, these techniques are costly and they still suffer from matrix effects when samples are analyzed directly. Spectroscopic interference and matrix effects in ICP-MS can be minimized or eliminated by careful selection of a suitable matrix separation technique prior to analysis. Therefore, for the determination of trace and ultratrace elements in complicated matrix samples by ICP-MS, separation/preconcentration steps prior to analysis are always necessary.

A number of separation/preconcentration procedures have been used for trace metal determinations: these include precipitation/co-precipitation [5], liquid–liquid extraction [6], and solid phase extraction (SPE) [7]. Among these techniques, SPE procedures, either off- or on-line, are considered superior to other procedures for their simplicity, consumption of small volumes of organic solvent, and ability to achieve a higher enrichment factor. The quest for new adsorbents is an important factor in improving analytical sensitivity and precision in SPE techniques. The main requirements for a substance to work effectively as an SPE adsorption material are as follows: it should consist of a stable and insoluble porous matrix having suitable active groups, typically organic groups, which can interact with analytes; it should achieve fast and quantitative sorption; and it should have high adsorption capacity, good regenerability, and surface area accessibility. To date, many adsorbents, such as active carbon [8], modified resin [9], nanometer-sized materials [10], and fullerene [11], have been employed in SPE. These adsorbents are normally modified by attaching organic and inorganic molecules to their surface. The resulting functional materials can work effectively to remove specific toxic metal ions from aqueous media.

Table 1
Isotopes of interest and potential polyatomic interferences in ICP-MS

Isotope	Potential interfering species
$^{63}\mathrm{Cu}$	$^{31}\mathrm{P}^{16}\mathrm{O}^{16}\mathrm{O}$, $^{40}\mathrm{Ar}^{23}\mathrm{Na}$, $^{47}\mathrm{Ti}^{16}\mathrm{O}$
$^{65}\mathrm{Cu}$	$^{49}\mathrm{Ti}^{16}\mathrm{O}$, $^{32}\mathrm{S}^{16}\mathrm{O}^{16}\mathrm{OH}$, $^{40}\mathrm{Ar}^{25}\mathrm{Mg}$
$^{111}\mathrm{Cd}$	$^{95}\mathrm{Mo}^{16}\mathrm{O}$, $^{94}\mathrm{Zr}^{16}\mathrm{OH}$, $^{94}\mathrm{Mo}^{16}\mathrm{OH}$
$^{112}\mathrm{Cd}$	$^{95}\mathrm{Mo}^{16}\mathrm{OH}$, $^{96}\mathrm{Zr}^{16}\mathrm{O}$, $^{96}\mathrm{Mo}^{16}\mathrm{O}$
$^{114}\mathrm{Cd}$	$^{114}\mathrm{Sn}$, $^{98}\mathrm{Mo}^{16}\mathrm{O}$, $^{97}\mathrm{Mo}^{16}\mathrm{OH}$
$^{202}\mathrm{Hg}$	$^{40}Ar\ ^{162}Dy$, $^{186}W^{16}O$
$^{208}\mathrm{Pb}$	$^{192}Pt^{16}O$, $^{40}Ar^{168}Yb$

Silica gel is an ideal support for SPE because it is stable under acidic conditions, does not swell, has high mass exchange characteristics, and shows very high thermal resistance. Furthermore, it is also abundant and inexpensive [8]. Immobilizing thiol ligand onto the surface of silica gel creates a material suitable for taking up heavy metals [12–14]. The effectiveness of such materials for binding metal ions is attributed to metal complexation by the thiols. However, traditional SPE using thiol-functionalized materials or other synthetic adsorbents is usually time-consuming when dealing with large volumes of sample. Moreover, these conventional adsorbents usually show poor recovery of the target metal ions from large volumes of solution because of the low binding capacity, diffusion limitations, and the lack of active surface sites. Hence, it would be of interest to develop a novel adsorbent with a large adsorptive surface area, low diffusion resistance, high adsorption capacity, and fast separation for large volumes of sample solution.

Recently, nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties [15]. The size range of nanoparticles is from 1 to almost 100 nm, which falls between the classical fields of chemistry and solid state physics. The relatively large surface area and highly active surface sites of nanoparticles enables them to have a wide range of potential applications, including shape-selective catalysis [16], chromatographic separations [17], sorption of metal ions [18], enzyme encapsulation [19], DNA transfection [20], and drug delivery [21]. Magnetic nanoparticles, a new kind of nanometer-sized material, are widely used in the fields of biotechnology and biomedicine for applications such as cell labeling and separation [22], magnetic resonance imaging (MRI) (as a contrast agent) [23], enzyme and protein separations [24], targeted drug delivery [25], and magnetic ferrofluids hyperthermia [26]. These particles are superparamagnetic, which means that they are attracted to a magnetic field, but retain no residual magnetism after the field is removed. Therefore, suspended superparamagnetic particles adhered to the target can be removed very quickly from a matrix using a magnetic field, but they do not agglomerate after removal of the field. Hu et al. [27] employed magnetic Fe_2O_3 nanoparticles as adsorption material for the removal and recovery of Cr(VI) from wastewater, and the adsorption capacity was found to be very high. However, it should be pointed out that pure inorganic nanoparticles (such as Fe_3O_4 and Fe_2O_3) can easily form large aggregates, which may alter their magnetic properties [24]. Moreover, these nanometer-sized metal oxides are not target-selective and are unsuitable for samples with complicated matrices [28]. Therefore, a suitable coating is essential to overcome such limitations.

In this study, silica-coated magnetic nanoparticles (SCMNPs) modified with γ-mercaptopropyltrimethoxysilane (γ-MPTMS) were synthesized by a sol-gel method. These magnetic nanoparticles were employed as an SPE adsorbent for separating and concentrating trace amounts of Cd, Cu, Hg, and Pb from biological and environmental samples. The levels of these elements were then determined by ICP-MS.