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Simultaneous preconcentration of bismuth and lead ions on modified magnetic core–shell nanoparticles and their determination by ETAAS

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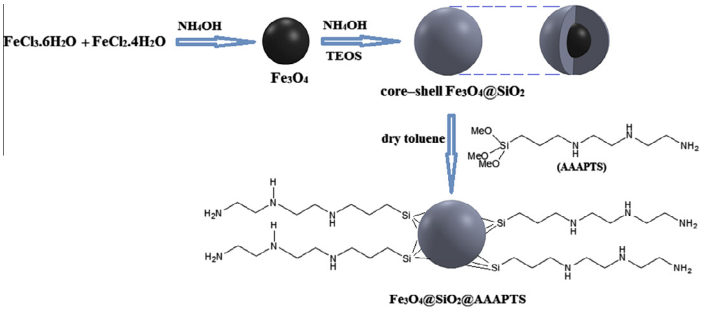
HIGHLIGHTS

- A new nanoadsorbent based on modified magnetic core–shell $Fe_3O_4@SiO_2$ was successfully prepared.
- It was used to extract bismuth and lead ions from various samples simultaneously.
- It is a very fast extraction method and exhibits very good adsorption capacity and analytical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic core–shell silica nanoparticles modified by 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (AAAPTS) were prepared and used as new adsorbent for simultaneous extraction and preconcentration of bismuth and lead ions through magnetic solid-phase extraction (MSPE) method. After adsorption, these ions were desorbed with nitric acid followed by determination with electrothermal atomic absorption spectrometry. Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) spectrometry and vibrating sample magnetometer (VSM) were used to characterize the adsorbent. The MSPE conditions were optimized. The detection limits of 1.4 and 3.7 ng L^{-1} were obtained for bismuth and lead, respectively. The linear range was 0.003–0.200 ng mL^{-1} for bismuth and 0.02–0.700 ng mL^{-1} for lead. The relative standard deviations of the method for eight replicate determination of 0.07 and 0.35 ng mL^{-1} of Bi(III) and Pb(II) were ±3.6% and ±3.1%, respectively. The method was applied for the determination of target ions in different samples with high recoveries.

1. Introduction

Nowadays, simultaneous extraction and preconcentration of several metal ions at trace levels from various real matrices has great importance [1]. In this work, a sensitive procedure for extraction and preconcentration of Bi(III) and lead(II) has been described simultaneously. Bismuth and its compounds have been used in many different areas such as cosmetic products, lubricating oils, medicines, pigments, electronics, semiconductors, alloys industry and in recycling of uranium nuclear fuels [2–4]. It is also found as a secondary component in some tin, copper and lead minerals [5]. Neuropathology, osteoarthropathy, nephropathy and hepatitis have been attributed to bismuth compounds as toxic effects in

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humans [6]. Lead is widely used in chemical and plastic industries, battery manufacturing, smelting, pigment products, printing industries and mining [7]. It is considered as dangerous toxic metal to the environment and human health [8]. The binding of Pb(II) to serum albumin is very strong and there are many binding site for the binding of Pb(II) on albumin protein. In addition, it affects the functional properties of albumin [9]. Accumulation of lead in the vital organs can cause poisoning, brain and kidney damage, anemia and cancer [10]. From this point of view, bismuth and lead have been distributed in environment increasingly. Therefore, the trace analysis of these metals is necessary. Several analytical methods, e.g. electrochemical methods [11], atomic absorption spectrometry [12–14], inductively coupled plasma-atomic emission spectroscopy [15] and etc. have been reported for the determination of Bi(III) and Pb(II). But, the direct determination of trace metal ions is often limited due to the low concentration and strong interference from the real sample matrices. To enrich the metal ion concentration and remove the target analytes from the sample matrices, a separation and preconcentration step such as coprecipitation [16], solvent extraction [17], cloud point extraction (CPE) [18], solid-phase extraction (SPE) [19,20] and magnetic solid-phase extraction (MSPE) [21,22] have been applied.

Recently, MSPE has been intensively used for environmental analysis at trace levels [21–24]. In this technique, magnetic nanoparticles (MNPs), as adsorbent, are served without any packing of cartridges. They are just added into a sample solution containing target analytes. After adsorption, MNPs can be easily removed from sample solution using a magnet placed outside of the extraction container. Therefore, the main advantages of MSPE include low price, rapidity, simplicity and reusability [24]. However, naked MNPs tend to form agglomerates, as well as, they are chemically active and oxidize in air, resulting in loss of magnetism [25]. Thus, it is necessary to coat them with inorganic layer such as silica or alumina [26]. Silica protective shell not only stabilize the MNPs, but can also be used for surface modification with specific compounds, for instance, a wide range of organic ligands or other functional groups, depending on the desired application [27–29].

3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (AAAPTS) is a reagent which is used to modify the surface of inorganic materials and organic polymers [30,31]. It has more amino groups with free lone pair of electrons on nitrogen atoms. Therefore, these atoms are suitable sites for coordination with metal ions effectively.

Here, we successfully prepared an adsorbent based on magnetic core–shell $Fe_3O_4@SiO_2$ nanoparticles modified with AAAPTS. Then, this adsorbent was applied in MSPE for preconcentration of Bi(III) and Pb(II) simultaneously prior to electrothermal atomic absorption spectrometric (ETAAS) determination.

2. Experimental

2.1. Reagents and apparatus

Stock solutions of bismuth and lead were prepared by dissolving of $Bi(NO_3)_3{\cdot}5H_2O$ and $Pb(NO_3)_2$ (Merck, Darmstadt, Germany) into deionized water. Working solutions were prepared daily by appropriate dilution of stock solutions. $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, NH_3, ethanol and HNO_3 were analytical grades and purchased from Merck Company. Tetraethyl orthosilicate (TEOS) for preparing silica shell on magnetic nanoparticles was also obtained from Merck. 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (Acros organics, New Jersey, USA) was used to prepare the modified adsorbent in this study. High purity reagents from Sigma (St. Louis, MO, USA) were used for studying interference effects.

Table 1
Instrumental parameters and thermal program of ETAAS for the determination of bismuth and lead ions.

Parameter	Bi	Pb
Instrumental parameters		
Wavelength (nm)	223.3	283.1
Spectral bandwidth (nm)	0.1	0.5
Lamp current (mA)	10	5
Signal measurement	Peak Height	Peak Height
Sample volume (μL)	20	20

Step	Furnace temp. (°C)		Time(s)	Argon flow rate (L min^{-1})
	Bi	Pb		
Drying	85	85	5.0	3.0
Drying	95	95	40	3.0
Drying	120	120	10	3.0
Ashing	400	400	6.0	3.0
Ashing	400	400	2.0	0.0
Atomization	2000	2100	1	0.0
Atomization	2000	2100	2.0	0.0
Cleaning up	200	2300	2.0	3.0

The concentrations of Bi(III) and Pb(II) were measured by a model Spectra AA 220 apparatus (Varian, Victoria, Australia) atomic absorption spectrometer with an electrothermal atomizer and autosampler. Optimum operating parameters for them are given in Table1. The samples were weighed using an electronic balance Mettler AE-160 (Greifensee, Switzerland). The pH measurements were carried out with a Metirohm 827 pH-meter (Herisau, Switzerland) supplied with a combined glass–calomel electrode. Magnetic stirrer hot plate and mechanical stirrer (2000 rpm) and oven model 100 (Memmert, Frankfurt, Germany) were used to homogenize. To disperse the nanoparticles in solutions, a Sonorex digitec model DT 225H with 35 kHz ultrasonicator (Bandelin, Berlin, Germany) was used. Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) in KBr were taken using a Tensor 27 spectrometer (Bruker, Saarbrucken, Germany) with spectral resolution better than 1 cm^{-1}. Field emission-scanning electron microscopy (FE-SEM) images were obtained on a model Hitachi S-4160 (Tokyo, Japan) with an accelerating voltage of 20 kV. The samples were loaded onto a glass surface previously sputter coated with a homogeneous gold layer for charge dissipation during the SEM imaging. A LEO 912AB transmission electron microscope (TEM), (Carl Zeiss Inc., Jena, Germany) was used with an accelerating voltage of 100 kV. Samples were first dispersed in water and then collected using carbon-film-covered copper grids for analysis. The powder X-ray diffraction (XRD) patterns were examined on a model X'PertPro diffractometer (Panalytical, Almelo, The Netherlands) using Cu Kα radiation (wavelength = 1.54 Å). The data were collected over a range of 10–80° 2θ with a step size of 0.01°, nominal time per step of 2 s and slit width 5 nm. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) model MDKFD (Danesh Pajohan Kavir Co. Kashan, Iran).

2.2. Preparation of Fe_3O_4 magnetic nanoparticles

The preparation of Fe_3O_4 magnetic nanoparticles was based on dissolving $FeCl_3{\cdot}6H_2O$ (11.68 g) and $FeCl_2{\cdot}4H_2O$ (4.30 g) in 200 mL deionized water. Then, this solution was stirred with mechanical stirrer (1000 rpm) at 80 °C for 30 min. Nitrogen gas was continually bubbled through this solution to expel oxygen. Following that, 25 mL of 25% NH_3 was rapidly added to the solution. After that, the color of bulk solution changed from orange to black immediately. The magnetite precipitates were collected by a magnet after