



Application of C₁₈-functional magnetic nanoparticles for extraction of aromatic amines from human urine



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ABSTRACT

In this paper, a novel method using C₁₈-functional ultrafine magnetic silica nanoparticles (C₁₈-UMS NPs) as adsorbents was developed for rapid extraction and enrichment of aromatic amines from urine. C₁₈-UMS NPs were prepared by chemical coprecipitation, silanization and alkylation. The aromatic amines can be adsorbed on C₁₈-UMS NPs and isolated easily from the matrix with an external magnetic field. After desorption with acetonitrile, the aromatic amines were determined by ultra fast liquid chromatography. The experimental parameters, such as pH value of sample solution, amount of C₁₈-UMS NPs, extraction time, type and volume of desorption solvent, and desorption time were optimized. The analytical performances of the present method were also evaluated. The limits of detection for 1-aminonaphthalene, 4-aminobiphenyl, 4,4'-diaminodiphenylmethane and 4-aminophenylthioether were 1.3, 0.88, 1.1 and 1.1 ng mL⁻¹, respectively. The results showed that the present method was simple, highly efficient and rapid for the extraction and enrichment of aromatic amines from urine.

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1. Introduction

There are various kinds of aromatic amines in the surrounding living environments, such as, aniline, benzidine, 4-aminophenylthioether, *p*-chloroaniline and so on [1,2]. They are toxic and carcinogenic. The concentration of aniline in drinking water is limited to 100 ng mL⁻¹ [3]. Aromatic amines are widely used as raw materials or intermediates in the manufacturing of industrial chemicals such as pesticides, pharmaceuticals, explosives, rubber, epoxy polymers, cosmetics, dye stuff plants and aromatic polyurethanes [4–6]. The concentration of these amines in textile and leather articles is limited to 30 μg g⁻¹ by European Union regulations [7]. In some other countries, the acceptable limits were lower, e.g., 20 μg g⁻¹ in textiles [8]. The uses of carcinogenic aromatic amines have caused great harm to human health [9]. Carcinogenic aromatic amines were detectable in several commercial hair dyes [10]. The known bladder carcinogen 4-aminobiphenyl (4-ABP) was detectable in several commercial hair dyes in levels up to 12.8 ng mL⁻¹ [11]. The use of aromatic amines can increase the risk of cancer because they can be easily absorbed through the skin. These aromatic amines, such as 4-ABP, are important carcinogenic agents in tobacco smoke [12]. Environmental tobacco smoke should be a source of aromatic amines. When the azo dyes were absorbed

by oral ingestion (particularly by babies sucking on toys and textiles containing these dyes) and through sweat or via friction with clothing, the azo dyes can be degraded to release aromatic amines in liver cells, extrahepatic tissue and epidermal cells [7]. The carcinogenic aromatic amines in the body can harm human health. The determination of aromatic amines in human urine is particularly important.

Wu et al. extracted and separated aromatic amines in lake water by solid phase microextraction (SPME) [13]. Dasgupta extracted aromatic amines by liquid-liquid extraction (LLE) [14]. However, the methods in these studies are time-consuming and organic solvent wasting. So it is necessary to develop a simple, rapid and reliable sample pretreatment method for the determination of aromatic amines.

Recently, magnetic nanoparticles (MNPs) have received increasing attention. Generally, MNPs are prepared by encapsulating inorganic magnetic cores (mainly Fe₃O₄ core) with organic polymer or inorganics [15,16]. Because of their large surface areas, unique physical and chemical properties, the MNPs have been widely used in many fields, such as biotechnology, biomedicine, protein separation, removal of metal ions and dyes [17–21]. The paramagnetic properties of these particles allow the easy isolation of products from solution by the external magnetic field. Thus, suspended MNPs tagged with analytes can be isolated from large volume samples using a magnet. The isolation and purification of the MNPs are easier and faster than those of other materials. In recent years, the MNPs were widely

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used in analytical chemistry. Parham et al. utilized magnetic iron oxide nanoparticles to extract fluoride in water samples [22]. Zhao et al. synthesized silica-magnetite nanoparticle mixed hemimicelle sorbents for rapid extraction of typical phenolic compounds from environmental water samples [23]. Gao et al. prepared magnetite-silica-poly(methacrylic acid-co-ethylene glycol dimethacrylate) sorbents and investigated the efficiency of these nanoparticles in extraction of sulfonamide in milk samples [24].

To the best of our knowledge, few papers have been reported on the use of MNPs to extract and preconcentrate analytes in human urine. In this study, C₁₈-functional ultrafine magnetic silica nanoparticles (C₁₈-UMS NPs) were synthesized by coating ultrafine Fe₃O₄ NPs with silica and subsequently immobilizing dimethyl octadecyl chlorosilane (OCS) on the nanoparticles. These MNPs were used for the extraction of aromatic amines in human urine based on magnetic solid-phase extraction (MSPE). Due to the high surface area and the excellent adsorption capacity of these MNPs, satisfactory extraction recoveries of aromatic amines could be achieved. The aromatic amines were analyzed by the ultra fast liquid chromatography (UFLC). C₁₈-UMS NPs show high performance potential in processing complicated samples.

2. Experimental

2.1. Chemicals

The standards of 1-aminonaphthalene (AN, *pK*_a, 3.92, *log P*, 3.2), 4-aminobiphenyl (4-ABP, *pK*_a, 4.35, *log P*, 2.9), 4,4'-diaminodiphenylmethane (4,4'-DADP, *pK*_a, 4.96, *log P*, 1.6) and 4-aminophenylthioether (4-APT) were obtained from J&K Scientific (Fig. S1). Appropriate amounts of the compounds were dissolved in methanol to prepare 500 μg mL⁻¹ stock standard solutions of each compound. Then the mixed stock solution containing all compounds (10 μg mL⁻¹) was prepared from individual stock standard solution by diluting with methanol and stored under dark condition at 4 °C. Dimethyl octadecyl chlorosilane (OCS) was supplied by Alfa Aesar (USA). Iron(II) chloride tetrahydrate (FeCl₂·4H₂O), iron(III) chloride hexahydrate (FeCl₃·6H₂O) and sodium hydroxide were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Chromatographic-grade methanol and acetonitrile were purchased from Fisher (New Jersey, USA). Analytical-grade toluene, triethylamine, *n*-hexane, ethanol, isopropanol, tetraethyl orthosilicate (TEOS), ammonia, hydrochloric acid were obtained from Beijing Chemical Works (Beijing, China). The deionized water was prepared with Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Preparation of C₁₈-functionalized ultrafine magnetic silica nanoparticles

The magnetic nanoparticles, C₁₈-functionalized ultrafine magnetic silica nanoparticles (C₁₈-UMS NPs), were synthesized by chemical coprecipitation, silanization and alkylation method. First, FeCl₂·4H₂O (1.0 g), FeCl₃·6H₂O (2.6 g) and HCl (12 mol L⁻¹, 0.425 mL) were added in 12.5 mL of deionized water. The mixture was added dropwise into 125 mL NaOH solution (1.5 mol L⁻¹) under vigorous stirring with nitrogen gas passing continuously through the solution. The reactor was placed into an 80 °C water bath and the mixture was stirred vigorously for 3 h. The obtained Fe₃O₄ NPs precipitate was separated from the reaction medium under the magnetic field and washed with 100 mL deionized water four times. The amount of Fe₃O₄ NPs was 1.0 g and the yield is 90.05% (in Fe content). Then, the newly prepared Fe₃O₄ NPs were added into a solution containing deionized water (6 mL), isopropanol (43 mL) and 1.25 mL of ammonia (25%, m/m). After stirring for 15 min with

nitrogen gas passing through the solution, TEOS (125 μL) was added into the solution. The resulting solution was then allowed to stand for 4 h at room temperature under continuous stirring. Then the magnetic silica nanoparticles were washed with deionized water three times and dried in a vacuum oven at 60 °C. The dried magnetic silica microspheres (0.6 g) were added into 30 mL of anhydrous toluene. The resulting mixture was heated to boiling, and then 0.6 mL of triethylamine and 0.9 g of OCS were added in the mixture. The mixture was then refluxed for 5 h. The obtained C₁₈-UMS NPs were washed and dried (Fig. S2a).

2.3. MSPE procedure

Firstly, 20 mL of filtered urine sample was adjusted to pH 9 by adding 2 mL of pH 9 phosphate buffer. 50 mg of C₁₈-UMS NPs was added into the urine sample. The mixture was stirred for 20 min. Subsequently, C₁₈-UMS NPs adsorbing aromatic amines were isolated with a strong magnet at the bottom of the container and the supernatant was poured out. The C₁₈-UMS NPs were washed with 1 mL of deionized water. C₁₈-UMS NPs adsorbing aromatic amines were placed in 3 mL of acetonitrile, and the resulting mixture was stirred for 1 min. The aromatic amines were eluted into acetonitrile. After the C₁₈-UMS NPs were removed, the eluate was dried under a stream of nitrogen at 50 °C and the residue was dissolved in 0.2 mL of methanol. 3 μL of this solution was injected into the UFLC system for analysis. When the mixture of methanol-water was used to dissolve the residue, the peaks shapes of aromatic amines were slightly better than those obtained with the methanol and the recoveries of aromatic amines slightly decreased. Finally, methanol was used to dissolve the residue (Fig. S2b). C₁₈-UMS NPs can be recycled by washing with methanol for 8 min, deionized water for 8 min and methanol for 10 min.

2.4. UFLC determination

The aromatic amines were separated and determined using an ultra fast liquid chromatographic (UFLC) system (Shimadzu Corporation, Kyoto, Japan) equipped with two LC-20AD pumps, a SIL-20A automatic sample injector, a CTO-20A column oven and a SPD-20A UV-vis detector. The separation was performed on a Shimadzu XR-ODS column (75 mm × 2 mm, 2.2 μm particle size). The mobile phase was the mixture of methanol and water (50:50, v/v) and the flow-rate was set at 0.2 mL min⁻¹. The monitoring wavelength was 240 nm for AN, 4,4'-DADP and 280 nm for 4-ABP, 4-APT. The temperature of column was controlled at 30 °C. Injection volume was 3 μL.

2.5. Human urine samples

The present method was applied to the analysis of urine samples from three donors (sample 1, sample 2, and sample 3) who are working in education and other two donors (sample 4 and sample 5) who are working in tobacco company. The mean age of urine human donors is 36.2. The samples were taken and immediately collected in sterilized 500 mL of polyethylene bottles. All urine samples were filtered through 0.45 μm nylon membranes (Shanghai Institute of Pharmaceutical Industry, China) and analyzed directly in triplicate. The spiked urine samples were prepared by adding standard solution of aromatic amines into the real urine samples.

3. Results and discussion

3.1. Characterization of C₁₈-UMS NPs

The synthesis of C₁₈-UMS NPs involves three steps: chemical coprecipitation, silanization and alkylation. Observation by

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