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ORIGINAL PAPER

In-tube solid-phase microextraction with a hybrid monolithic column for the preconcentration of ultra-trace metals prior to simultaneous determination by ICP-MS

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Abstract

The preparation of an amino-functionalized hybrid monolithic column (TEOS-*co*-AEAPTES) via one-pot co-condensation of tetraethoxysilane (TEOS) and N-(β-aminoethyl)-γ-aminopropyltriethoxysilane (AEAPTES) in a capillary is descibed. It was used as solid-phase microextraction (SPME) matrix followed by inductively coupled plasma-mass spectrometry (ICP-MS) for determination of trace metals. Under optimum conditions, the amino-functionalized SPME material can simultaneously retain Cu(II), Zn(II), Au(III), and Pb(II) with adsorption capacities of 148, 60, 81, and 64 μg m^{-1}, respectively. Subsequently, these four metal ions can be quantitatively eluted using 1 mol L^{-1} HNO_3 containing 1% thiourea. The retention mechanism of Cu(II), Zn(II), Au(III), and Pb(II) on the amino-functionalized hybrid monolith was explained as the combination of electrostatic and coordination interactions. With a 10-fold enrichment factor, the calibration curves were established in the range 0.5–100 μg L^{-1} with linear correlation coefficients above 0.9943 and the limits of quantitation were 0.05 μg L^{-1} for four target analytes. The limits of detection were 0.006, 0.012, 0.004, and 0.007 μg L^{-1} for Cu(II), Zn(II), Au(III), and Pb(II), respectively. The protocol was validated by analyzing Certified Reference Materials including standard sediment, soil, and nickel ore, and the results were in good agreement with their certified values. The relative standard deviations of the method were in the range 0.22–17.6%. The recoveries of the four metal ions in spiked samples were in the range 88.0–113.8%. Compared to direct ICP-MS determination, the proposed in-tube SPME procedure can effectively eliminate the interference from complex matrix, especially from those ores with very high content of main metal to improve the accuracy of analysis. Therefore the method is suitable for the simultaneous determination of ultra-trace Cu(II), Zn(II), Au(III), and Pb(II) in environmental and mineral samples.

Keywords Hybrid monolithic column · Amino-functionalization · Solid-phase microextraction · Trace metals · ICP-MS

Introduction

Metal elements such as copper and zinc are essential and integral trace elements for life [1]. Lead is a highly toxic element which can accumulate in the organism because of biological magnification in the natural environment [2]. Although gold is scarce and stable in nature [3], long-term use of gold-containing products may have a potential impact on human health [4]. Therefore, it is of great significance to analyze these trace metals in environmental samples [5]. Besides, since the existence and level of some characteristic elements, whether macro or trace, reflect important region information of minerals, determination of the abundances of ultra-trace metals in mineral samples is of critical meaning for their source recognition. Because the attention for trace metal elements has been continuously increasing [6], it is quite essential to establish selective, sensitive, and accurate analytical

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methods for the simultaneous quantification of multiple metals in environmental and mineral samples.

Up to now, there are plenty of techniques for the analysis of metal elements [7–10]; ICP-MS is most commonly applied in the determination of trace metals in environmental and mineral samples due to its advantages of wide linear range, high sensitivity, and simultaneous detection of multiple elements [10]. However, direct analysis of real samples by ICP-MS still faces some problems. The concentration of some target metals in environmental and mineral samples is very low not to be directly determined, and that is easily contaminated. On the other hand, the analysis of these environmental and mineral samples by ICP-MS suffers from mass spectrum and non-mass spectrum interference resulted from matrix effect [11]. Isobaric overlap, polyatomic or compound ions, refractory oxide ions, and double charge ions all cause mass spectrum interference [12]. For mineral samples, a significant problem to surmount is the severe memory effect that is apparent for high concentration of main metal of ore in the instrument, leading to non-linear calibration graphs, long washout times, decreasing sensitivity with time, and signals dependent on the matrix. Even worse, the metallic mineral matrix not only causes inaccurate measurement results, but also damages mass spectrometer and even causes instrument contamination or flameout [13]. Therefore, efficient sample pretreatment methods are generally required before ICP-MS analysis for real environmental and mineral samples.

Solid-phase extraction (SPE) is one of the frequently used techniques for the preconcentration of trace metal ions [14]. Recently, as a late model solid-phase microextraction extraction (SPME) material, capillary monolithic columns have attracted extensive attention because of their less sample consumption, uniform structure, controllable morphology, convective mass transfer, and excellent adsorption performance [15, 16]. The SPME performed within a capillary tube is also named as in-tube SPME or capillary microextraction (CME) [2]. Monolithic columns include inorganic silica [17], organic polymer [18], and organic-inorganic hybrid monolithic columns [19]. Organic-inorganic hybrid monolithic columns are extensively exploited for separation because of their low-swelling, high mass-exchange, large specific surface area, and high mechanical stability [20]. “One-pot” is a facile preparation procedure for hybrid monolithic column which means functional groups are introduced directly into the monolith in the process of co-condensation of organosilane reagents with tetra-alkoxysilanes. Hybrid monolith prepared via one-pot condensation can make functional groups distributed more evenly and preparation process simpler. Although the application of organic-inorganic hybrid monolithic columns has shown great success in organic and biological analysis fields [21–23], only a few works related to them have been conducted in the determination of trace elements and their speciation in environmental samples [24, 25]. Moreover, there are not any reports to utilize hybrid monolithic material as SPME matrix for enriching trace metal elements from high main metal ores prior to ICP-MS determination.

In this present work, organic-inorganic hybrid monolithic column (TEOS-*co*-AEAPTES) prepared via one-pot process by sol-gel technology in a fused capillary was applied for simultaneous SPME of Cu(II), Zn(II), Au(III), and Pb(II) followed by ICP-MS determination. The adsorption and elution conditions of these four metal ions were optimized comprehensively. The interaction mechanism between target ions and amino-functionalized monolith was explained accordingly. The analytical figures of merits were also concluded to further prove the reliability of the method. Finally, the application potential of TEOS-*co*-AEAPTES monolith was investigated as SPME absorbent for ICP-MS determination of Cu(II), Zn(II), Au(III), and Pb(II) in environmental waters, sediments, soils, coals, and iron ores.

Materials and methods

Reagents and materials

Tetraethoxysilane (TEOS, 98%) was purchased from Alfa Aesar (Tianjin, China). N-(β-aminoethyl)-γ-aminopropyltriethoxysilane (AEAPTES, 98%) and thiourea (99+%) were purchased from Ourchem (Shanghai, China). Cetyltrimethylammonium bromide (CTAB, 98+%) was purchased from TCI (Tokyo, Japan). Nitric acid was of guaranteed reagent grade and purchased from Merck (Zurich, Switzerland). All other chemicals were at least of analytical reagent grade and used without further purification. Pure water (18.25 MΩ cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout the experiment.

Stock solutions (1 mg mL^{-1}) of Cu(II), Zn(II), and Pb(II) were prepared by dissolving appropriate amounts of $Cu(NO_3)_2{\cdot}2H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and $Pb(NO_3)_2$ (National Institute of Metrology, Beijing, China), respectively, in 2% (v/v) diluted HNO_3. Stock solution (1 mg mL^{-1}) of Au(III) was prepared by diluting 1000 mg mL^{-1} of $HAuCl_4$ solution (National Research Center for Certified Reference Materials, Beijing, China). Lower concentration standard solutions were prepared daily by appropriate dilutions from their stock solutions. Analytical mixture standard solution (each of 1 mg L^{-1}) containing Cu(II), Zn(II), Au(III), and Pb(II) was prepared by mixing and diluting the above four stock solutions.

Certified Reference Materials of GBW07309 sediment (GSD-9) and GBW07402 soil (GSS-2) were purchased from Institute of Geophysical and Geochemical Prospecting for Certified Reference Materials (Langfang, China). Certified Reference Material of GBW(E)070110 nickel ore (Fe, 46.99%) was purchased from the National Research Center for Certified Reference Materials. Tap water was collected in the Chemical Building in Xianlin Campus of Nanjing University. River water was taken from Yangtze River in Nanjing. Both water samples were stored with 2% (v/v) HNO_3. Soil was taken from Gulou Campus of Nanjing University, and sampling of soil is given in the Electronic Supporting Material (ESM). All mineral samples were provided by the Technical Center for Industrial Product and Raw Material Inspection and Testing, Shanghai Customs (Shanghai, China). Water samples were filtered through a 0.45 μm cellulose acetate membrane before analysis. Sediment, soil, coal, and iron ore samples were digested with nitric acid, hydrogen peroxide, and aqua regia before analysis [26]. The detailed procedure is given in the ESM.

Instrumentation

The determination of four target elements including ^{63}Cu, ^{66}Zn, ^{197}Au, and ^{208}Pb was performed on a Perkin-Elmer NexION 350D ICP-MS (Perkin-Elmer SCIEX, Concord, Canada) and the optimum operation conditions are summarized in Table S1. The pH values of solutions were controlled by a FiveEasy Plus pH meter (Mettler-Toledo, Shanghai, China). During the extraction process, a syringe infusion pump (LSP04-1A, LongerPump, Hebei, China) was used to introduce solution into the monolithic column.

Scanning electron microscopy (SEM) images were recorded with a Hitachi S-3400 II SEM (Hitachi, Tokyo, Japan). Fourier-transform infrared (FT-IR) spectra were collected on a NEXUS 870 FT-IR spectrometer (Nicolet, USA) using KBr pellets. Elemental analysis (EA) of the monolith was carried out using an Elementar Vario EL II elemental analyzer (Elementar, German) with oxygen as the combustion gas. Pore size distribution was investigated by a mercury intrusion porosimeter (Poremaster GT-60, Quantachrome, USA). The surface area was calculated using mercury intrusion porosimetry methods.

Preparation of TEOS-*co*-AEAPTES hybrid monolithic column

The TEOS-*co*-AEAPTES monolithic capillary was prepared by the procedures reported previously [27, 28] with minor modifications, as detailed in the ESM.

SPME and analysis procedure

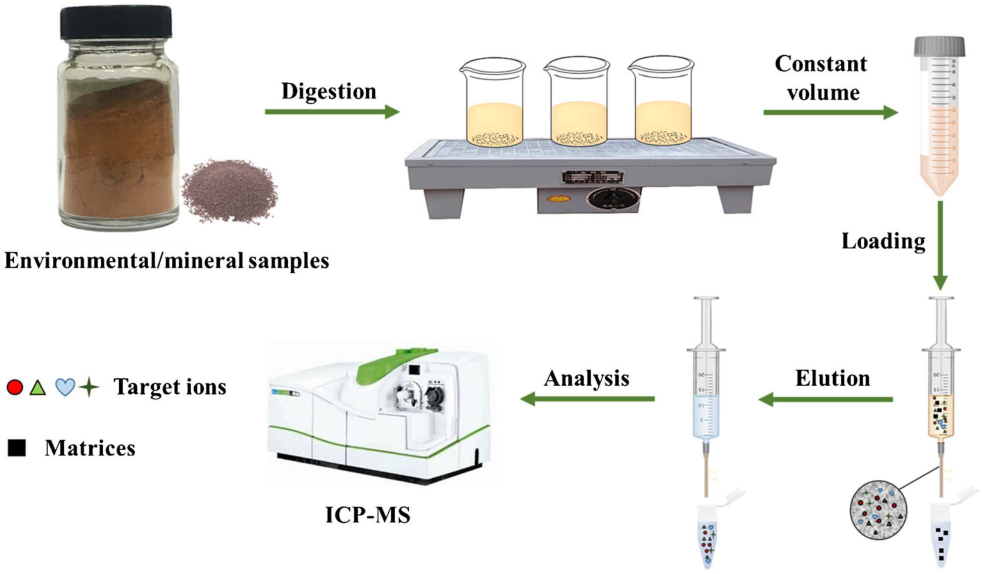
The TEOS-*co*-AEAPTES monolithic capillary was used as SPME matrix during Cu(II), Zn(II), Au(III), and Pb(II) enrichment procedure (Scheme 1) prior to ICP-MS detection. The pH of sample solution was adjusted to 4.5 with HNO_3 or $NH_3 \cdot H_2O$. In the extraction step, 3 mL solution (pH 4.5) was allowed to pump through the TEOS-*co*-AEAPTES column at a flow rate of 150 μL min^{-1}. Subsequently, 300 μL of mixture of 1 mol L^{-1} HNO_3 with 1% (m/v) thiourea was used as eluent to syringe the analytes retained on the monolithic capillary at the same flow rate. Both effluents obtained during the loading and elution processes were collected and four analytes were measured simultaneously by ICP-MS. Purified water was adjusted to pH 4.5 as the blank sample.

Results and discussion

Choice of materials and metal ions

The extraction efficiency of SPE/SPME depends mainly on the properties of the adsorption materials. According to the Lewis acid-base theory, there is a high affinity between transition metal ions as Lewis acid and ligands containing amino as Lewis base. Therefore, extraction matrices with amino-containing functional group have high adsorption efficiency towards metal ions [28, 29]. Inspired by this knowledge, three amino-functional monomers including aminopropyltriethoxysilane (APTES), AEAPTES, and [(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AAAPTES) were considered in this study. It was found that AEAPTES had the best solubility in the solvent system of the experiment. The obtained monolith prepared by AEAPTES was uniform and porous, which was suitable for the extraction of metal ions. The octanol-water partition coefficients (logP) of APTES, AEAPTES, and AAAPTES calculated by ACD ChemSketch were -0.22 ± 0.44, -0.71 ± 0.56, and 1.07 ± 0.55, respectively. Therefore, AEAPTES was the most hydrophilic among the three amino-functional monomers, which supported the experimental results. As mentioned, hybrid monolith prepared via one-pot condensation can make functional groups distributed more evenly and preparation process simpler. Consequently, TEOS-*co*-AEAPTES hybrid monolithic column prepared via one-pot method was employed to investigate the extraction of trace metal ions.

The existence and level of some characteristic elements including Cu(II), Zn(II), Au(III), and Pb(II) prevalent in environmental and mineral samples can reflect important region information. The extraction feasibility of the prepared TEOS-*co*-AEAPTES hybrid monolithic column towards the characteristic metal ions in environmental and mineral samples was investigated. It was found that Cu(II), Zn(II), Au(III), and Pb(II) can be quantitatively adsorbed in the same weakly acidic condition (pH 4.0–6.0). Therefore, these four ions were selected as the target analytes in this study. The preparation of the TEOS-*co*-AEAPTES monolithic column and the SPME procedure of Cu(II), Zn(II), Au(III), and Pb(II) under optimal conditions are shown in Scheme S1 in the ESM.



Scheme 1 Sample pretreatment and SPME-ICP-MS analysis process

Characterization of hybrid monolithic column

As the SEM photographs at different magnifications showed, the TEOS-*co*-AEAPTES skeletons formed were homogeneous and also attached to the inner surface of the fused silica capillary tightly. Even better, no apparent voids along the inner wall of capillary could be observed (Fig. 1a, b). The monolith possessed continuous macroporous structure and interconnecting spheres with uniformly small size of particles and rough surface (Fig. 1c, d). Therefore, the well-controlled skeleton of the monolith was beneficial to the formation of high surface area, low back-pressure, and high permeability. The diameter size of the pore of the TEOS-*co*-AEAPTES monolith was analyzed by mercury intrusion porosimetry to be 3 μm (Fig. S1), and the average surface area was calculated 15 m^2 g^{-1}. In addition, in order to examine the mechanical stability of the monolithic capillary, the pressure variation of the column was recorded at different flow rates of methanol

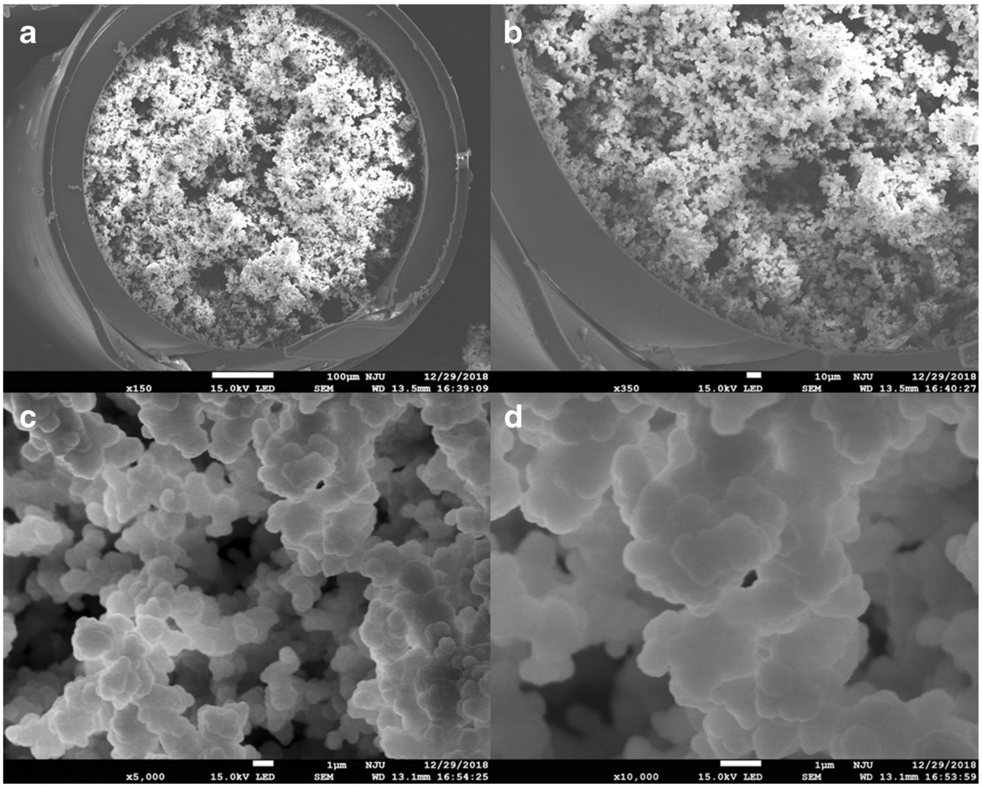


Fig. 1 SEM images of the TEOS-*co*-AEAPTES hybrid monolithic column (**a** × 150; **b** × 350; **c** × 5.00 k; **d** × 10.0 k)

(Fig. S2). The pressure was linearly increased in the tested flow rate range, which revealed that the column had low back-pressure and excellent mechanical strength.

FT-IR spectrum of the organic-inorganic hybrid monolith is shown in Fig. 2. The absorption bands around 1058 cm^{-1} corresponded to the stretching vibrations of Si-O-Si groups. The strong peaks around 1472 and 1638 cm^{-1} resulted from the C-N and N-H stretching vibrations, respectively. The appearances of adsorption bands around 2925 and 3375 cm^{-1} were ascribed to the vibration of C-H and O-H, respectively. All above indicated that the amino-silane group from AEAPTES had been incorporated into the monolith. Moreover, thermal analysis including TGA and DSC proved the incorporation of AEAPTES in the matrix (Fig. S3). TGA showed that the weight loss process could be divided into three stages, and the proportion of each stage was approximately 7.5%:7.5%:10%, which was consistent with the decomposition of AEAPTES. There were two sharp peaks in the DSC curve between 200 and 400 °C, which was related to the decomposition of amino groups. In addition, EA data showed the presence of carbon and nitrogen elements derived from organosilane reagents (Table S2). In conclusion, all of the characterization results proved that the amino-functionalized monolithic capillary had been successfully synthesized.

Optimization of analysis procedure

Optimization of adsorption condition

The pH of aqueous solution plays a significant role in adsorption process [21, 24]. In this work, the effect of the pH of 1 mL aqueous solution on the adsorption percentages of 30 μg L^{-1} Cu(II), Zn(II), Au(III), and Pb(II) on the TEOS-*co*-AEAPTES monolithic column was investigated with pH varying in the range of 1.0–8.0. It could be observed in Fig. 3 that in the relatively wide pH range of 3.0–8.0, four studied metals were quantitatively adsorbed by TEOS-*co*-AEAPTES monolithic column. At pH below 3.0, the amino-functionalized monolith had a positively charged surface due to protonation of amino groups (NH_3^+), leading to electrostatic repulsion between amino and metal ions including Cu^{2+}, Zn^{2+} and Pb^{2+}. On the contrary, NH_3^+ on the monolith had certain electrostatic attraction towards $AuCl_4^-$, making partial gold ions absorb on the column. When the pH increased from 3.0 to 8.0, the functional groups on the monolith changed from NH_3^+ to NH_2, the electrostatic attraction interaction gradually disappeared, and instead, the coordination interaction between NH_2 and Cu^{2+}, Zn^{2+}, and Pb^{2+} dominated. In addition, there was a strong affinity between NH_2 and Au^{3+}, so NH_2 could replace Cl^- and coordinate with Au^{3+}, resulting in the adsorption of Au^{3+} on the AEAPTES monolith. Since the metal ions might be hydrolyzed at the higher pH than 6.0 [30], solution pH was adjusted to 4.5 for the further experiments.

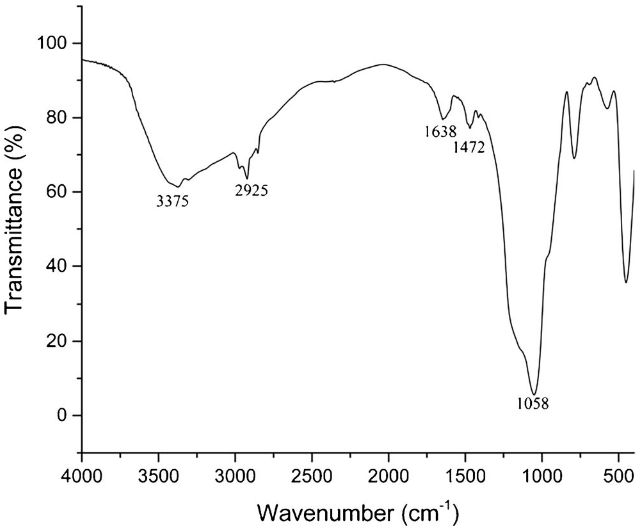


Fig. 2 FT-IR spectrum of TEOS-*co*-AEAPTES monolith

Other adsorption conditions including the sample flow rate and solution volume [2, 24] were investigated with the results shown in Fig. S4 and S5, respectively. In short, the following experimental conditions were found to give optimal results: (a) Sample pH value 4.5; (b)Flow rate 150 μL min^{-1}; (c) Solution volume 3 mL.

Optimization of elution condition

Strong acids were selected as the eluents at the beginning in view of the result of dependence of adsorption rate on pH (Fig. 3). The result in Fig. 4a showed that either 1 mol L^{-1} HNO_3 or HCl can elute Cu(II), Zn(II), and Pb(II) successfully, except Au(III). Due to the electrostatic attraction interaction between

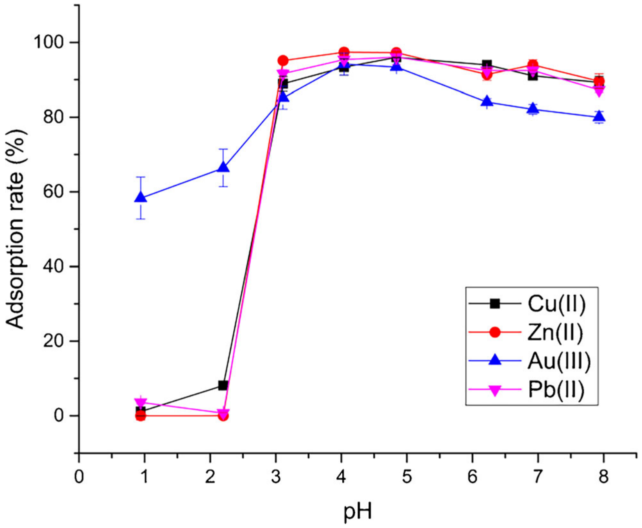


Fig. 3 Adsorption rates of Cu(II), Zn(II), Au(III), and Pb(II) on TEOS-*co*-AEAPTES monolithic column under different pH. Concentration of each metal ions, 30 μg L^{-1}; Sample volume, 1 mL

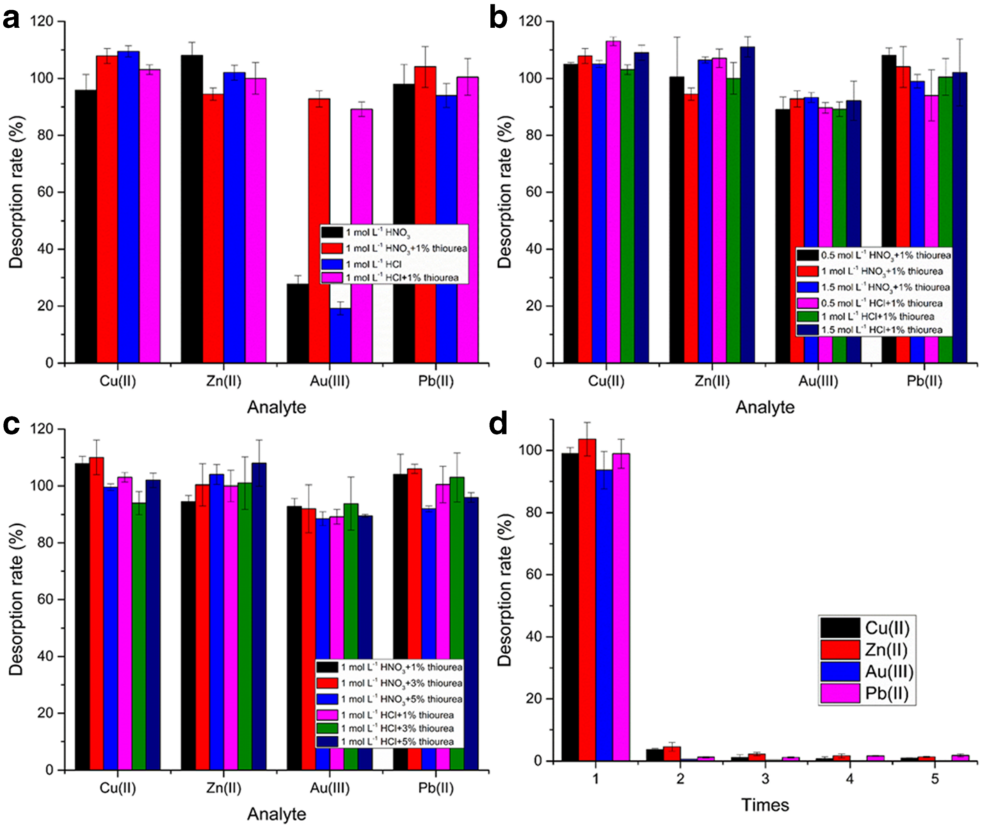


Fig. 4 Effect of eluent on the desorption rates of Cu(II), Zn(II), Au(III), and Pb(II). **a** Effect of eluent composition; **b** Effect of nitric acid or hydrochloric acid concentration (0.5, 1, and 1.5 mol L^{-1} HNO$_3$/HCl with 1% thiourea); **c** Effect of thiourea concentration (1 mol L^{-1} HNO$_3$/HCl with 1%, 3%, and 5% thiourea); **d** Effect of elution times, 300 μL eluent (1 mol L^{-1} HNO$_3$ with 1% thiourea) each time. Concentration of each metal ions in sample solution, 30 μg L^{-1}; Sample volume, 3 mL; Solution pH, 4.5; Eluent volume of **a**, **b**, and **c**, 1 mL

$AuCl_4^-$ and the protonated amino groups at very low pH, it was difficult to release Au(III) from amino-functionalized monolith utilizing acids only. Therefore, thiourea was added to the eluent according to its good affinity to Au(III) [31]. As could be seen, the desorption effects of all four metal ions were excellent when 1% (m/v) thiourea was added in the eluent. In Fig. 4b, there was no obvious difference in the desorption effect of Cu(II), Zn(II), Au(III), and Pb(II) while changing the acid concentration. All these ions could be quantitatively eluted when the concentration of thiourea varying from 1% to 5% with HNO$_3$/HCl concentration fixing at 1 mol L^{-1} (Fig. 4c). Consequently, 1 mol L^{-1} HNO$_3$ with 1% thiourea was employed for the elution of all target ions in the following experiments. The effect of elution volume on desorption rate of target ions was also optimized. A total of 1500 μL eluent (1 mol L^{-1} HNO$_3$ with 1% thiourea) was continuously used to desorb Cu(II), Zn(II), Au(III), and Pb(II) from the TEOS-*co*-AEAPTES monolithic column and the effluent was collected each 300 μL. The result in Fig. 4d distinctly indicated that the initial 300 μL eluents were plentiful for desorbing all target ions from the column. Comprehensive considering the experimental efficiency and enrichment factor, the eluent being as less as better, the elution volume was ultimately set to 300 μL when the sample consumption was 3 mL with the enrichment of 10 times for target ions. The desorption rates of Cu(II), Zn(II), Au(III), and Pb(II) did not change obviously during experiment of elution flow rate varying in the range of 20–300 μL min^{-1} (Fig. S6). The result was similar to the flow rate experiment of adsorption. As a result, the elution flow rate we employed in this research work was determined as 150 μL min^{-1}.

Adsorption capacity of TEOS-*co*-AEAPTES monolithic column

Adsorption capacity is a significant indicator to evaluate the performance of SPME material. The breakthrough curve experiment recommended by Hu et al. [32] was carried out in this present work. In order to investigate the maximum adsorption capacity of TEOS-*co*-AEAPTES monolithic column for four target ions, 15 mL solutions containing each target metal ion (1 mg L^{-1}, pH 4.5) were continuously pumped through the 5-cm length monolithic column at 150 μL min^{-1}, respectively. Then, the concentration of target ion in the effluent was determined by ICP-MS. When the adsorption of an ion by the monolithic column was saturated, the concentration of the ion in the effluent suddenly increased and approached the initial concentration. The breakthrough curves were shown in Fig. S7 and the maximum adsorption capacities of the monolithic column for Cu(II), Zn(II), Au(III), and Pb(II) were 148, 60, 81, and 64 μg m^{-1} with the relative standard deviations (RSDs) of 1.0%, 2.2%, 1.6%, and 1.1%, respectively, which were much higher than subsequent application needs.

The reproducibility and reusability of TEOS-*co*-AEAPTES monolithic column

The reproducibility of TEOS-*co*-AEAPTES monolithic columns was evaluated by investigating the recoveries of 30 μg L^{-1} solution containing four target metal ions under the optimized conditions with six segments of monolithic capillary prepared in the same batch and different batches. The results in Table S3 indicated that the intra-batch RSDs of the preparation reproducibility of monolithic column ranged from 1.8% (Cu(II)) to 7.3% (Zn(II)) and the inter-batch RSDs ranged from 2.4% (Pb(II)) to 8.1% (Zn(II)). Furthermore, the prepared monolithic column can be reused for six times at least because the recoveries of Cu(II), Zn(II), Au(III), and Pb(II) did not decrease obviously during six successive repeating experiments with the RSDs of 4.0%, 8.1%, 0.47%, and 1.8%, respectively (Fig. S8). In addition, the stability of the columns stored for different duration (freshly prepared, stored for 1 week, 2 weeks, and 4 weeks) was also evaluated under the same conditions, and the RSDs ($n = 4$) of the recovery rates ranged from 4.8% (Cu(II)) to 7.7% (Zn(II)). The experiments verified excellent repeatability and stability of the amino-functionalized hybrid monolithic capillary.

Interference study

The possible coexisting ions in environmental and mineral samples may compete with the analytes for the active sites of the amino-functionalized monolith, especially the ore samples that were rich in a variety of high level main metals. Thus, the interference effects of coexisting ions were investigated as follows. 3 mL aqueous solution containing Cu(II), Zn(II), Au(III), and Pb(II) each at 5 μg L^{-1} with a certain concentration of coexisting ion was subjected to the general SPME-ICP-MS procedure. The results in Table 1 indicated that the recoveries of four target ions were in the range of 84.3–108.9% in the presence of 25 mg L^{-1} of Na^+, 25 mg L^{-1} of K^+, 10 mg L^{-1} of Fe^{3+}, 1 mg L^{-1} of Ca^{2+}, Al^{3+}, Mg^{2+}, Ni^{2+}, and Mn^{2+}. In addition, main anions such as SO_4^{2-}, NO_3^-, and Cl^- with the concentration of 10 mg L^{-1} and PO_4^{3-} of 1 mg L^{-1} did not change the recoveries obviously. It demonstrated that the prepared TEOS-*co*-AEAPTES monolithic column had a relatively good tolerance to the coexisting interference and maintained adsorption capacity of target ions at a high concentration of interfering ions. According to the main components of the real samples that had been digested already, the presence of major interfering ions and their concentrations were included in this interference study. Furthermore, the important interference components in the real samples were focused. For example, the concentration of Fe^{3+} in the SPME effluent was 18.3% of the initial concentration, which indicated that the matrix interference could be effectively reduced by the TEOS-*co*-AEAPTES monolithic column. Therefore, the SPME-ICP-MS protocol had an excellent anti-interference ability for the determination of ultra-trace Cu(II), Zn(II), Au(III), and Pb(II) in environmental and mineral samples of complex matrices.

Analytical performance of SPME-ICP-MS method

The analytical performance of the developed TEOS-*co*-AEAPTES monolith based SPME-ICP-MS method was evaluated under the optimized conditions. The calibration curves established in the range of 0.5–100 μg L^{-1} for Cu(II), Zn(II), Au(III), and Pb(II) equations were $Y = 10.245X - 0.1289$, $Y =$

Table 1 Interference effects of diverse ions (mean ± SD, $n = 3$)

Coexisting ion	Concentration (mg L^{-1})	Recovery (%)			
		Cu(II)	Zn(II)	Au(III)	Pb(II)
Na^+	25	102.5 ± 3.3	104.0 ± 0.1	94.1 ± 1.3	95.6 ± 1.8
K^+	25	102.7 ± 0.9	95.3 ± 1.5	89.0 ± 1.8	108.9 ± 0.2
Fe^{3+}	10	93.3 ± 0.4	89.8 ± 1.1	88.4 ± 4.8	95.6 ± 1.0
Mg^{2+}	1	101.7 ± 3.4	105.0 ± 1.9	84.3 ± 4.3	103.8 ± 0.4
Mn^{2+}	1	99.4 ± 6.1	103.1 ± 1.4	86.2 ± 1.3	100.7 ± 0.9
Al^{3+}	1	106.9 ± 0.1	93.4 ± 3.7	91.2 ± 0.8	104.2 ± 2.3
Ni^{2+}	1	97.1 ± 6.4	103.4 ± 1.4	91.2 ± 3.5	105.4 ± 1.4
Ca^{2+}	1	97.3 ± 0.9	99.6 ± 9.2	87.7 ± 0.4	105.9 ± 1.8
NO_3^-	10	96.7 ± 0.9	97.3 ± 1.5	97.0 ± 1.8	93.9 ± 0.2
Cl^-	10	102.7 ± 0.9	95.3 ± 1.5	89.0 ± 1.8	108.9 ± 0.2
SO_4^{2-}	10	102.5 ± 3.3	104.0 ± 0.1	94.1 ± 1.3	95.6 ± 1.8
PO_4^{3-}	1	107.2 ± 0.2	95.4 ± 2.4	97.9 ± 6.5	97.5 ± 4.2

Table 2 An overview on recently reported nanomaterial-based methods for preconcentration and determination of metal ions

Materials	Methods	Tolerance level of Fe^{3+} (mg L^{-1})	LODs of analyte (μg L^{-1})				Application	Ref.
			Cu(II)	Zn(II)	Au(III)	Pb(II)		
APTES-silica monolithic column	CME-ICP-MS	5	0.006	–	–	0.014	Rice flour, human hair and urine	[2]
AAPTS-silica monolithic column	CME-ICP-MS	10	0.002	0.012	–	–	Human hair, serum and urine	[33]
Down-sized chelating resin-packed minicolumn	SPE-ICP-MS	–	0.0003	0.0007	–	0.0001	Seawater	[34]
Nanometer-sized alumina	SPE-ICP-MS	2	0.045	0.078	–	0.027	Lake samples, coal fly ash, rice flour, rye grass	[35]
TEOS-*co*-AEAPTES monolithic column	In-tube SPME-ICP-MS	10	0.006	0.012	0.004	0.007	Water, sediment, soil, coal, iron ore	This study

$9.3065X - 0.2218$, $Y = 9.7406X + 0.3544$, and $Y = 9.8710X + 0.2647$, respectively with r^2 of 0.9972, 0.9992, 0.9958, and 0.9943, and the limits of quantitation (LOQs) were 0.05 μg L^{-1} for these ions. The limits of detection (LODs, defined as 3-fold the standard deviation of blank signal intensity) of Cu(II), Zn(II), Au(III), and Pb(II), with 10-fold enrichment factor, were 0.006, 0.012, 0.004, and 0.007 μg L^{-1}, respectively for water samples, and 0.008, 0.016, 0.005, and 0.009 μg g^{-1}, respectively for sediment, soil, coal, and ore samples. Therefore, this protocol is quite suitable for ultra-trace metal analysis of environmental and mineral samples.

For comparison, the analytical performance of the method and other related approaches reported in the literature for Cu(II), Zn(II), Au(III), and Pb(II) analysis is listed in Table 2. The proposed method has relatively lower LODs for all target ions and lower than most methods reported. The method can analyze four target ions at the same time with high analysis efficiency, while the work about analysis of Au(III) based on similar materials has been rarely reported. In addition, the proposed method can be applied to more kinds of real samples with complex matrices. Although the monolith did not have the ability to extract a certain metal ion specifically like ion-imprinted materials, and anti-interference test should be carefully carried out, the proposed method can eliminate the interference from those ores with extremely high content of main metal, which is very meaningful for accurate analysis of multiple characteristic trace ions in environmental and mineral samples.

The accuracy of the proposed method was verified by determining trace Cu(II), Zn(II), Au(III), and Pb(II) in Certified

Table 3 Contents of Cu(II), Zn(II), Au(III), and Pb(II) in Certified Reference Materials and real environmental and mineral samples

Samples	Content (mg kg^{-1})							
	Cu(II)		Zn(II)		Au(III)		Pb(II)	
	Mean ± SD	RSD (%)	Mean ± SD	RSD (%)	Mean ± SD	RSD (%)	Mean ± SD	RSD (%)
GSD-9	29.8 ± 1.1	3.7	72.7 ± 3.1	4.3	ND	–	24.7 ± 0.7	2.8
(Certified)	(32 ± 2)		(78 ± 4)		(NA)		(23 ± 3)	
GSS-2	17.2 ± 2.7	15.7	44.1 ± 1.7	3.9	ND	–	21.5 ± 1.1	5.1
(Certified)	(16.3 ± 0.9)		(42 ± 3)		(NA)		(20 ± 3)	
GBW(E)070110	126.5 ± 4.5	3.6	194.6 ± 14.0	7.2	ND	–	22.2 ± 1.0	4.5
(Certified)	(120 ± 20)		(230 ± 20)		(NA)		(23 ± 2)	
Tap water*	5.09 ± 0.23	4.5	48.99 ± 0.11	0.22	ND	–	0.98 ± 0.02	2.0
Yangtze River water*	4.96 ± 0.26	5.2	6.56 ± 1.10	0.17	ND	–	1.46 ± 0.16	0.11
Soil (Nanjing)	14.6 ± 0.7	4.8	41.0 ± 1.2	2.9	ND	–	22.3 ± 1.3	5.8
Russia coal	5.5 ± 0.2	3.6	25.8 ± 0.5	1.9	ND	–	9.1 ± 0.1	1.1
Indonesia coal	19.6 ± 0.8	4.1	12.0 ± 0.6	5.0	ND	–	1.7 ± 0.3	17.6
Burma iron ore	814.0 ± 28.0	3.4	196.0 ± 17.0	8.7	ND	–	83.0 ± 4.0	4.8
Kazakhstan iron ore	733.0 ± 19.0	2.6	446.0 ± 19.5	4.4	ND	–	25.5 ± 1.5	5.9

* Concentration, μg L^{-1}

Reference Materials of GSD-9 (Sediment), GSS-2 (Soil) and GBW(E)070110 (Nickel ore). The results summarized in Table S4 indicated that the determined values of these target metals were in accordance with the certified values, which further proved the reliability of this protocol. However, if the nickel ore was directly determined by ICP-MS after digestion and simple dilution without SPME pretreatment, the results of four target elements greatly differed from the certified values (Table S5). This is likely attributed to the strong interference of high concentration of main metal ions in the sample solution. It was interestingly found that most of the interfering ions in the ore could be eliminated by the SPME procedure with the prepared amino-functionalized hybrid monolith capillary. For example, 82.4% Fe^{3+} and 78.6% Ni^{2+} in the digestion solution were removed after SPME by detecting them in the effluent. Therefore, this TEOS-*co*-AEAPTES monolithic column can not only effectively achieve the preconcentration of target ions but also powerfully reduce the interference from the main metals in ores.

Furthermore, the proposed method was applied to the analysis of environmental water, soil, coal, and iron ore samples from different sources. The determination results for Cu(II), Zn(II), Au(III), and Pb(II) were also listed in Table 3, indicating good precision of the method with the RSDs of 0.22–17.6%. The recoveries of four metal ions spiked in these environmental and mineral samples were summarized in Table S6. The recoveries of four target ions in all spiked samples were obtained 88.0–113.8%, demonstrating that the proposed SPME-ICP-MS protocol could be used in the simultaneous determination of ultra-trace elements in real environmental and mineral samples.

Conclusions

TEOS-*co*-AEAPTES hybrid capillary monolithic column prepared via one-pot was employed for the SPME of Cu(II), Zn(II), Au(III), and Pb(II) in environmental and mineral samples. The adsorption mechanism of four metal ions was explained as the combination of electrostatic and coordination interactions based on the transformation of NH_2 and NH_3^+ at different pH. Notably to Au(III), there exists a competing coordination between amino group and chloride ion under pH 3.0–5.0. The purposed SPME-ICP-MS method possessed strong anti-interference ability, simple preparation and reusability, low sample consumption, and high efficiency of analysis. Although the proposed method was limited in specificity, it can effectively reduce miscellaneous matrix interference in complex samples, when simultaneous multi-element analysis was performed. To our knowledge, this work is the first time to apply organic-inorganic hybrid monolithic capillary for the determination of ultra-trace elements in complex environmental and mineral samples, especially in the ores with very high content of main metal.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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