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Preconcentration of trace aluminum (III) ion using a nanometer-sized TiO$_2$-silica composite modified with 4-aminophenylarsonic acid, and its determination by ICP-OES

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Abstract We describe a nanometer sized composite material made from titanium dioxide and silica that was chemically modified with 4-aminophenylarsonic acid and used for selective solid-phase extraction, separation and preconcentration of of aluminum(III) prior to its determination by ICP-OES. Under optimized conditions, the static adsorption capacity is 56.58 mg g^{-1}, the enrichment factor is 150, the relative standard deviation is 1.6% (for $n=11$), and the detection limit (3 s) is 60 pg mL^{-1}. The method was validated by analyzing the reference materials GBW 09101 (hair) and GBW 10024 (scallop) and successfully applied to the determination of trace Al(III) in spiked water samples and human urine, with recoveries ranging from 96% to 101%.

Keywords 4-aminophenylarsonic acid modified nano-TiO$_2$/SiO$_2$ composite material · Preconcentration · Aluminum (III) · ICP-OES

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Introduction

Aluminum is a non-essential element to which humans are frequently exposed. Aluminum is widespread throughout nature, air, water, plants and consequently in all the food because of its wide use [1]. The determination of very low levels of aluminum has become increasingly very important in environmental and clinical chemistry since its negative roles in the human life. During recent years, interest concerning aluminum has considerably increased due to the knowledge about potential toxic effects of aluminum [2–5]. Therefore, preconcentration and selective separation of trace or ultra-trace aluminum from food, biological and natural water is very important and need much more attention. Inductively coupled plasma optical emission spectrometry is the most used technique in determining of trace elements because of the capability for rapid multi-element detection over a wide concentration range with relatively low detection limits. However, it is really difficult to determine elements directly at low concentrations or on samples with complicated matrices by using ICP-OES. Because of this, separation and preconcentration of trace aluminum prior to ICP-OES determination is essential.

Many preconcentration techniques have been proposed for determining trace aluminum in water and various environmental samples. Currently, the most commonly used techniques for preconcentration and separation of trace elements include liquid–liquid extraction [6, 7], solid-phase extraction [8–10], ion exchange [9], and single drop microextraction [11], etc. Solid-phase extraction (SPE) technique becomes more popular compared with traditional liquid–liquid extraction method. The SPE has several major advantages which include (i) higher enrichment factor, (ii)

much easier operation, (iii) safety with respect to hazardous samples, (iv) higher selectivity, (v) lower cost and less time, (vi) and more flexible to combine with others different modern detection techniques in the form of on-line or offline mode [12]. The choice of appropriate sorbent is a critical factor to obtain full recovery and high-enrichment factor in the SPE procedure. Numerous substances have been proposed and applied as solid-phase extractants, such as activated carbon [13], XAD resins [14, 15], Chromosorb 101 [16], modified silica gel [17, 18], cellulose [19], eggshell membrane [20] and ion exchange resins [21].

Nowadays, nanometer TiO_2, a new solid material becomes more important due to its special physical and chemical properties [22]. One of nanoparticle's properties is that most of the atoms are on the surface. The surface atoms are unsaturated and therefore can bind other atoms that possess highly chemical activity. There have been reports in the literature on the preconcentration and separation of trace elements in biological samples by means of nanometer TiO_2 material [23–27]. But, some heavy metal cations are poorly adsorbed on nanometer TiO_2 when pH value is less than 6 [24, 25]. Although some metals cations can be adsorbed on nanometer TiO_2 when pH value is equal or more than 8, they are more likely to be precipitated under the higher pH value.

As can be seen from the above, they mostly used untreated or modified nanometer TiO_2 as a SPE sorbent, and the selectivity for metal ions was quite poor. In order to improve the selectivity and adsorption capacity, nanometer TiO_2/SiO_2 composite material is normally modified by attaching organic and inorganic compounds which comprise heteroatom such as oxygen, nitrogen, sulfur and phosphorus to their surface. So, it is expected that nanometer TiO_2/SiO_2 composite material modified with organic compounds would be more selective than untreated nanometer TiO_2/SiO_2 for the solid-phase extraction of metal ions. To the best of our knowledge, it has been sparingly reported so far.

We describe a nanometer sized composite material made from titanium dioxide and silica that was chemically modified with 4-aminophenylarsonic acid and used for a new sorbent. A solid phase extraction method using the new sorbent has been developed to separate and concentrate trace Al(III) from aqueous samples. The sorbent presented high selectivity and adsorption capacity for the solid phase extraction of trace Al(III). Parameters that affect the sorption and elution efficiency of trace Al(III) were studied in batch and column modes. Then, the method was applied to test trace Al(III) from actual samples. The analytical precision and accuracy of the method were achieved with satisfied results, and the method was convenient to use. The procedure was validated by standard addition and analysis of a standard reference material (GBW 09101 hair and GBW 10024 scallop).

Experimental

Instrumentation

An Iris Advantage ER/S inductively coupled plasma emission spectrometer, Thermo Jarrel Ash (Franklin, MA, USA) was used for all metal ions determination. The instrumental parameters were those recommended by the manufacturer. The wavelength selected for Al(III) was 396.1 nm. A pHs-4C digital pH meter, Shanghai Lei Ci Device Works (Shanghai, China) was used for the pH adjustments. An YL-110 peristaltic pump, General Research Institute for Non-ferrous Metals, (Beijing, China) was used in the column process. A PTFE (polytetrafluoroethylene) column (50 mm×9.0 mm i.d, Tianjin Jinteng Instrument Factory, Tianjin, China) was used. Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR apparatus (U.S.A).

Standard solutions and reagents

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was used throughout.

methyl-trimethoxysilane(Hangzhou Yiyuan Biochemical Co. LTD., Hangzhou, China), titanium tetraisopropoxide (Wuxi Yangshan Biochemical Co. LTD., Wuxi, China, http://www.yschemicals.com), 4-Aminophenylarsonic acid (The Third Reagent Factory, Shanghai, China, http://www.reagent.com.cn/), and 3-aminopropyltrimethoxysilane (APS, Qingdao Ocean University Chemical Company, Qingdao, China) were used to prepare sorbent.

Stock standard solution of Al(III) at a concentration of 1.000 mg mL^{-1} was obtained from the National Institute of Standards (Beijing, PR China, http://www.gbw114.org). Working standard solutions were obtained by appropriate dilution of the stock standard solutions.

The reference material (GBW 09101 hair and GBW 10024 scallop) was purchased from National Research Center for Certified Reference Materials (Beijing, China http://www.nrccrm. org.cn/eng/index_en.asp).

Sample preparation

Jialinjiang and Changjiang water were collected from Jialinjiang and Changjiang, Chongqing, China. All water samples were filtered through a 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China), and acidified to a pH of about 2 with concentrated HCl prior to storage for use. Tap water samples taken from our research laboratory were analyzed without pretreatment. The pH value was adjusted to 2 with 0.10 mol L^{-1} HCl prior to use.

Portions (0.5000 g) of standard reference material of human hair (GBW 09101, PR China) were transferred into PTFE beakers, 10 mL of concentrated HNO_3 and 3 mL of H_2O_2 were added, heated until the solution become transparent, continuously heated to near dryness. The residue was dissolved in 0.10 mol L^{-1} HNO_3 and made up to 50 mL with distilled water. For preparation of human urine, 1.0 mL urine was transferred into 50 mL volumetric and diluted to the mark with distilled water.

Pig liver was purchased from HuaLian supermarket, ChongQing, China. All vegetable samples were purchased from JialeFu supermarket, ChongQing, China. Pig liver, GBW 10024 scallop and vegetable leaves were dried in an oven at 80 °C to constant weight. A 1.000 g pig liver, GBW 10024 scallop and vegetable leaves samples were weighted and transferred to a digestion tube, and then 5 mL of concentrated HNO_3 were added into it, respectively. The tube was left at room temperature for one night. Then it was placed in a digester block and heated slowly until the temperature was up to 165 °C. This temperature was maintained until ceasing the evolution of brown fumes. After the tube was cooled down, 1.3 mL perchloric acid was added into it. Then the temperature was raised to 210 °C until evolution of white fumes begins. The volume was adjusted to 100 mL with doubly distilled deionized water when the tube was cooled down. After digestion, each sample solution was determined by procedure.

Preparation of 4-aminophenylarsonic acid modified Nano-TiO_2/SiO_2 composite material

Preparation of SiO_2 spheres

2.5 mL of methyl-trimethoxysilane was added to 100 mL of 1.0×10^{-4} mol L^{-1} nitric acid aqueous solution that was heated to 60 °C while vigorous stirring was maintained. Then 2.5 mL ammonia was added to the solution. A milky silica solution was attained. SiO_2 powder was extracted by centrifuging the milky suspension of silica, and the supernatant removed.

Preparation of TiO_2 sols

10 mL of titanium tetraisopropoxide was added dropwise into 200 mL acidic water containing 2 mL nitric acid and 20 mL acetic acid under vigorous stirring. Then the mixture was refluxed at 60 °C while stirring for 20 h.

Preparation of Nano- TiO_2/SiO_2 composite material

Silica gel powder was added to different relative weight percentages of TiO_2 sols. Then the mixture was dispersed in an ultrasonic bath for 15 min. The TiO_2/SiO_2 mixture was kept for 24 h to form TiO_2 grafted on SiO_2 spherical core–shell structure. The suspension mixture then was filtered and calcined in air at 500 °C for 3 h [28].

Preparation of modified 4-Aminophenylarsonic Acid Nano-SiO_2/TiO_2 composite material

10.0 g of nano-TiO_2/SiO_2 was suspended in 150 mL dry toluene containing 10 mL of 3-aminopropyltrimethoxysilane and refluxed over night. The product was filtered off, washed with toluene, ethanol and diethyl ether and dried in an oven at 60 °C for 6 h. The product was nano-TiO_2/SiO_2-Amine.

A 5.0 g amount of nano-TiO_2/SiO_2 Amine was suspended in 250 mL of dry toluene under stirring and heating, then 1.0 g of 4-Aminophenylarsonic Acid was added into the suspension and refluxed for 8 h. The product was filtered off, washed with ethanol and dried in an oven at 80 °C for 8 h.

General procedures

Batch method

A series of standards or sample solutions containing Al(III) was transferred into a 25 mL beaker, and the pH value was adjusted to the desired value with 0.10 mol L^{-1} HCl or 0.10 mol L^{-1} $NH_3 \cdot H_2O$. Then the volume was adjusted to 10 mL with doubly distilled deionized water. 20 mg of nano-TiO_2/SiO_2-4-Aminophenylarsonic acid was added, and the mixture was shaken vigorously for 15 min to facilitate adsorption of the metal ions onto the TiO_2/SiO_2-4-Aminophenylarsonic acid. After the solution was centrifuged, the concentrations of Al(III) in the solution was directly determined by ICP-OES.

Column SPE procedure

A total of 50 mg of nano-TiO_2/SiO_2-4-Aminophenylarsonic acid was packed in the PTFE column plugged with a small portion of glass wool at both ends. Before use, 0.50 mol L^{-1} HCl and doubly distilled deionized water were sequentially passed through the column to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Al(III) was prepared, and the pH values were adjusted to the desired pH with 0.10 mol L^{-1} HCl or 0.10 mol L^{-1} $NH_3 \cdot H_2O$. Each solution was passed through the column at a flow rate of 1.5 mL min^{-1} by using a peristaltic pump. Afterwards, the metal ions retained on microcolumn were eluted with 0.50 mol L^{-1} HCl. The analytes in the elution were determined by ICP-OES.

Results and discussion

FT-IR spectra

FT-IR spectra were obtained from TiO_2/SiO_2, TiO_2/SiO_2-ATP and TiO_2/SiO_2-ATP-4-Aminophenylarsonic acid. According to FT-IR spectra of TiO_2/SiO_2, the peaks at 3419.91 cm^{-1} correspond to the stretching vibration of TiO_2/SiO_2-OH unit. The peaks at 1039.26 and 465.72 cm^{-1} are attributed to Si-O-Si bonds. The peak at 1630.28 cm^{-1} corresponds to the bend vibration of zeolite water [29]. Comparison of the FT-IR spectra of TiO_2/SiO_2-ATP with ATP, a new peak (1494.74 cm^{-1}) appeared in TiO_2/SiO_2-ATP due to N-H bending vibration, which indicated the TiO_2/SiO_2-bound amine was prepared successfully. When TiO_2/SiO_2-ATP was modified by 4-Aminophenylarsonic acid, several new peaks appeared in the spectrum. According to the literature [30, 31], the new peaks can be assigned as follows: the peak at 1629.51 cm^{-1} is due to C=N stretching vibration. The weak bands in the range 1380.15–1538.11 cm^{-1} are due to the benzene ring characteristic vibrations in 4-Aminophenylarsonic acid. The bands around 3367.10 cm^{-1} can be assigned to O-H stretching vibration. Consequently, the above experimental results suggest that nano-TiO_2/SiO_2 was successfully modified by 4-Aminophenylarsonic acid.

Influences of pH

Solution acidity has two effects on metal adsorption: proton in acid solution can protonate binding sites of the chelating molecules, and hydroxide in basic solution may complex and precipitate many metals. Therefore, pH value is the first parameter to be optimized.

Therefore, in order to evaluate the effect of pH, according to procedures (Bath method), fifteen metal ions, viz. Cu(II), Ca(II), Mg(II), Ba(II), Mn(II), Cd(II), Co(II), Cr(III), Fe(III), Hg(II), Zn(II), Pb(II), Ni(II), Al(III) and Ga(III) were adsorbed by 20 mg sorbent and determined in different pH value (pH 1.0–8.0). As shown in Fig. 1, the adsorption percentage increases with the increase of pH and
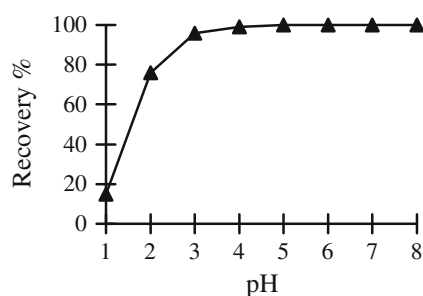
the metal recovery values of Al(III) was higher than other ions in range of (pH 1.0–8.0). To avoid hydrolyzing at higher pH, pH 3.0 was selected as the enrichment acidity in following experiments.

In addition, Cu(II), Ca(II), Mg(II), Ba(II), Mn(II), Cd(II), Co(II), Cr(III), Fe(III), Hg(II), Zn(II), Pb(II), Ni(II), Ga(III) were not adsorbed by sorbent at pH 3.0; Fe(III) and Ga(III) could be adsorbed by sorbent about 15–25% at pH 3.0, but they do not interfere with enrichment and determination of Al(III).
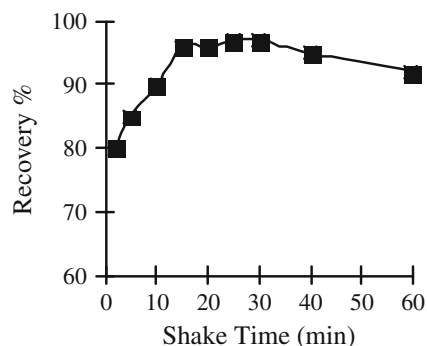
Al(III) was not enriched by bare nano-TiO_2/SiO_2 composite material at pH 3.0. The results have presented that the unique selectivity and adsorption quantity of nano-TiO_2/SiO_2-4-aminophenylarsonic acid for the solid-phase extraction of Al(III) improved obviously when nanometer TiO_2/SiO_2 composite material were modified by 4-aminophenylarsonic acid.

Effect of nano-TiO_2/SiO_2-4-Aminophenylarsonic acid mass

The amount of nano-TiO_2/SiO_2-4-Aminophenylarsonic acid is also important factor on the study for the quantitative adsorption of Al(III). The effect of amount of solid phase on the adsorption of Al(III) at optimum pH was investigated in the range 5–50 mg. The results showed that the adsorption of Al(III) gradually increased, up to 25 mg of solid phase and reached plateau. Therefore, 20 mg of nano-TiO_2/SiO_2-4-Aminophenylarsonic acid was selected for further studies.

Effect of shaking time

The shaking time is an important factor in determining the possibility of application of the on the new synthesized phases for the selective extraction of metal ions. At this work, different shaking time (rang from 2 to 60 min) was studied for the percentage extraction of Al(III) by nano-TiO_2/SiO_2-4-Aminophenylarsonic acid. As shown in Fig. 2,

Fig. 1 Effect of pH on analyte recovery; Al(III): 1.0 µg mL^{-1}; sample volume: 10 mL; flow rate: 1.5 mL min^{-1}, sorbent amount: 20 mg

Fig. 2 Extraction percentage of Al(III) at different shaking time ($N=$ 3); pH: 3.0; sample volume: 10 mL; flow rate: 1.5 mL min^{-1}; sorbent amount: 20 mg
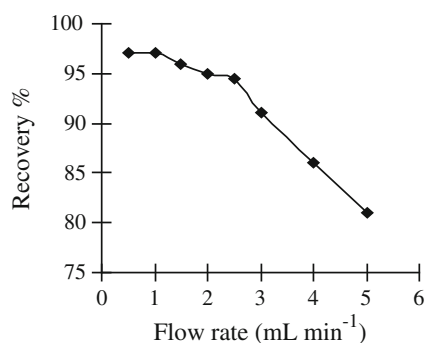
Fig. 3 Effect of flow rate on analyte recovery; Al(III):1.0 µg mL^{-1}; pH: 3.0; sample volume: 10 mL; sorbent amount: 20 mg

the adsorption of Al(III) was over 95% during the first 5 min, which indicates that kinetics of equilibrium is very fast. We selected 15 min for further studies.

Influence of elution condition on recovery

Since the adsorption of cations at $pH<1$ is negligible, one can expect that elution will be favoured in acidic solution. The elution condition was investigated by the batch and column procedure where various concentrations and volumes of HCl and HNO$_3$ solution were used for the desorption of retained Al(III). The obtained results show that 2.0 mL of 0.50 mol L^{-1} HCl was sufficient for 95% recovery for the target metal ion with a shaking time of 30 min. Accordingly, 2.0 mL of 0.50 mol L^{-1} HCl was used as eluent in the subsequent experiments.

Maximum sample volume and enrichment factor

The sample volume is one of the most important parameters to obtain high preconcentration factors for the analysis of a real sample [16]. The effect of sample volume on the retention behavior of the analyte on nano-TiO$_2$/SiO$_2$-4-Aminophenylarsonic acid was studied by varying the sample volume from 50 to 500 mL containing Al(III). It was found that the sample volume does not affect quantitative recovery of Al(III) in the range of 25–

300 mL of the sample volume. At the higher volumes than 300 mL, the recovery for Al(III) were decreased. Therefore, 300 mL of sample solution was adopted for the preconcentration of Al(III) from sample solutions. And a high enrichment factor of 150 was obtained because 2.0 mL of 0.50 mol L^{-1} HCl was used as eluent in these experiments.

Effect of the flow rate of the sample solution

As the retention of elements on adsorbent depends upon the flow rate of the sample solution, its effect was examined under the optimum conditions (pH, eluent, etc.) by passing 50 mL of sample solution through the micro-column with a peristaltic pump. The flow rates were adjusted within the range of 0.50 to 5.0 mL min^{-1}. The sorption of Al(III) was practically not changed up to 1.5 mL min^{-1} flow rate. It was found from Fig. 3, when the flow rates were over 1.5 mL min^{-1}, the recoveries of the analytes were less than 95%, as target metal ion could not equilibrate properly with the sorbent beds. Thus, the flow rate of 1.5 mL min^{-1} was selected in the column experiment.

Adsorption capacities

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate a specific amount of metal ions from the solution [32]. 20 mg of sorbent was equilibrated with 10 mL of various concentrations (50–400 µg mL^{-1}) of Al (III) for 1 h at pH 3. The separation and preconcentration procedures (*Batch* method) described above were applied. A break-through curve was gained by plotting the concentration (µg mL^{-1}) vs. the micrograms of Al(III) adsorbed per gram of nano-TiO$_2$/SiO$_2$-4-Aminophenylarsonic acid. From the experiment data, it was found that the maximum adsorption capacity of nano-TiO$_2$/SiO$_2$-4-Aminophenylarsonic acid for Al(III) up to 56.58 mg g^{-1}. The adsorption capacity of nano-TiO$_2$/SiO$_2$-4-Aminophenylarsonic acid for Al(III) was also compared with those of other important matrices used for the separation and preconcentration (Table 1). As seen from the data, nano-TiO$_2$/SiO$_2$-4-

Table 1 Figures of merit of comparable methods for determination of Al(III) by solid-phase extraction

Absorbent	Complexing media	Capacity mg g^{-1}	LOD ng mL^{-1}	EF	Ref.
Nano-TiO$_2$	8-Hydroxyquinoline	5.23	1.96	50	[25]
XAD-4 resin	Cetyltrimethylammo-niumbromide	4.4	4.9	–	[32]
XAD-1180/pyrocatech-ol violet	–	6.45	0.021	150	[33]
1-(2-pyridylazo)-2-nap-hthol (PAN)	Triton X-114		0.06	34.8	[9]
Silica gel	glycerol	0.4	2	500	[34]
Nano-TiO$_2$/SiO$_2$ composite material	4-aminophenylarsonic acid	56.58	0.06	150	This work

LOD Limit of detection; *EF* Enrichment factor

Aminophenylarsonic acid had a relatively high capacity compared to other methods reported.

Stability and reusability tests

To test the stability and reusability, the new sorbent was subjected to several loading and elution bath operations. The sorption conditions are referenced according to the above experiments. The elution operations were carried out by shaking the sorbent with 20 mL of 0.50 mol L^{-1} HCl together for 1 h so as to ensure complete equilibration. Then the sorbent was treated with double distilled water until neutral equilibration was reached. The operating capacity was calculated from the loading and elution tests. The results from three tests yielded <5% error up to 16 cycles of repeated experiments. The sorbent showed better long-term stability and reusability towards Al(III).

Effects of potentially interfering ions

The effects of different cations and anions on the adsorption of Al(III) on nano-TiO_2/SiO_2-4-Aminophenylarsonic acid were investigated. In these experiments, solutions of 1.0 μg mL^{-1} of Al(III) containing the added interfering ions were treated according to the recommended procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 90%. The results showed that in excess of 5,000—fold Na^+, K^+, NO_3^-, SO_4^{2-}, Cl^-; 1,000—fold Ca^{2+}, Mg^{2+}; 100—fold Mn^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}; 20-fold Cr^{3+}, Fe^{3+} ions had no significant interferences in the preconcentration and determination of Al(III). This is due to the low adsorbing capacity or rates for interfering ions. It can be seen that the presence of major potentially interfering ions has no obvious influences on the determination of Al(III) under the selected conditions.

Detection limits and precision

Under the selected conditions, eleven portions of standard solutions were analyzed simultaneously following the general procedure. The relative standard deviations (R.S.D.) is 1.6%, which indicated that the method had good precision for the analysis of trace Al(III) in solution samples. The detection limit (3σ) for Al(III), as defined by IUPAC, was 0.06 ng mL^{-1}.

Application

The method (Column SPE procedure) has been applied to the determinations of trace Al(III) in actual samples. Reference materials (GBW 09101 hair and GBW 10024 scallop) was used for method validation. In the analysis of

Table 2 Analytical results of Al(III) determination in biological and vegetable samples (μg g^{-1}) (N=3)

Sample	Certified value	Found by proposed method
GBW 09101(hair[a])	13.3±2.3	13.4±2.1
Pig liver		8.72±0.68
GBW 10024(scallop[a])	156±27	157±28
Cole		29±2.2
Celery		36±3.0
Caraway		31±2.8

[a] National research center for certified reference materials (Beijing, China)

actual samples, the standard addition method was used. The analytical results were given in Tables 2 and 3. The results indicated that the recoveries were reasonable for trace analysis in the range of 96–101%. It indicates that the method is reliable.

Conclusions

We describe a nano-TiO_2/SiO_2 composite material modified by 4-aminophenylarsonic acid showed a high adsorption and desorption property with respect to Al(III) as a solid-phase extractant. This composite sorbent was successfully applied to the separation/preconcentration of trace amount of Al(III) from aqueous solution without significant interference from other cations and anions. The method was simple and at low cost. The determination of Al(III) in the certified reference material showed good accuracy. The precision and accuracy of the method are satisfactory.

Table 3 Determination of Al(III) (ng mL^{-1}) in biological and water samples

Sample	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Changjiang River	0	22.7±0. 9	–
	10.0	32.4±1.2	97
	20.0	42.5±1.8	99
Jiaqlinjiang River	0	17.3±0.7	–
	10.0	26.9±1.3	96
	20.0	37.1±1.5	99
Tap Water	0	5.7±0.4	–
	10.0	15.5±0.9	98
	20.0	25.9±1.3	101
Human urine	0	23.2±1.1	–
	10.0	32.9±1.2	97
	20.0	43.1±1.7	100

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