

Trace Rare Earth Element Detection in Food and Agricultural Products Based on Flow Injection Walnut Shell Packed Microcolumn Preconcentration Coupled with Inductively Coupled Plasma Mass Spectrometry

Yan Li,^{*,†,§} Jia-lin Yang,[§] and Yan Jiang[§]

[†]College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecule, Tianjin Normal University, 393 Binshui West Road, Tianjin 300387, China

[§]Research Center for Analytical Sciences, Department of Chemistry, Nankai University, Tianjin 300071, China

S Supporting Information

ABSTRACT: With the extensive use of rare earth elements (REEs) in agriculture as fertilizer and feed additives, the concentration of REEs has increased in environmental and biological samples and finally impaired human health by food chain accumulation. The determination of trace REEs has gained considerable importance because of their toxicity and increasing occurrence. In this work, walnut shell has been used as the green adsorbent in online preconcentration and detection of REEs in food and agricultural products coupled with inductively coupled plasma mass spectrometry (ICP-MS). Because of the porous surface and abundant $-\text{COO}^-$ groups on the walnut shell surface, the walnut shell-packed microcolumn provides high adsorption efficiency and high tolerable capacity for coexisting ions. Under the optimized conditions, the adsorption efficiency of the walnut shell packed microcolumn was as high as 98.9% for 15 REEs, and the tolerable concentration ratios were between 2000 and 80 000 000 for 37 kinds of coexisting interfering ions. The enhancement factors achieved were 79–102 for 15 REEs with a sample loading volume of 4.7 mL. The detection limits were in the range of 2–34 pg g^{-1} . The relative standard deviation for 11 replicate preconcentrations of 2.5 ng L^{-1} REEs solution ranged from 0.5 to 2.0%. The present method was successfully applied to selective determination of REEs in 4 environmental and biological certified reference materials and 18 locally collected food and agricultural products.

KEYWORDS: rare earth elements, food and agricultural products, powdered walnut shell, inductively coupled plasma mass spectrometry

INTRODUCTION

In recent years, rare earth elements (REEs), owing to their specific characteristics, are attracting more and more attention in industry, such as electronics, superconductors, catalysts, and ceramics. Meanwhile, because they can promote the growth of plants and the body weight gain of animals, REEs are also widely used in agricultural and animal production as microelement fertilizer and feed additives.^{1,2} As a result, REEs are found at increased concentration into the environment and finally enter the bodies of human beings via the food chain.³ Moreover, continuous exposure to low concentrations of REEs could cause adverse health effects because of their bioaccumulation along the food chain. Chronic exposure to REE dust probably causes occupational pneumoconiosis.⁴ Long-term intake of low-dose REEs may lead to accumulation in the bone structure, changes in the bone tissue, and aberration of bone marrow cells and even bring about the generation of genetic toxicity in bone marrow cells.⁵ The REE ions may also impair the stability of DNA and even cause DNA damage.⁶ REEs can invade the central nervous system because they are susceptible to cerebral cortex and cause subclinical damage.⁷ Besides, it was reported that lanthanum aggravated the inhibitory amino acid receptor-mediated response in the sacral dorsal commissural nucleus,⁸ Tb^{3+} inhibited ATPase activity by binding to the high-affinity Ca^{2+} and Mg^{2+} binding sites,⁹ and Nd had a significant

inhibitory effect on the secretion of progesterone.¹⁰ The median lethal dose (LD_{50}) was reported between 10 and 7650 mg kg^{-1} for different kinds of REE metals or their different types of compounds.^{4,11} The toxicity of REEs is thus being paid more and more attention in food nutrition and food safety, and thus the determination of trace concentrations of REEs in various matrices has attracted considerable interest.

Owing to very low REE concentrations and the complex matrix, sophisticated analytical techniques have been developed for the determination of trace REEs in environmental, biological, and food samples, such as neutron activation analysis (NAA),¹² X-ray fluorescence (XRF),¹³ isotopic dilution mass spectrometry (IDMS),¹⁴ inductively coupled plasma atomic emission spectrometry (ICP-AES),^{15–17} and ICP-MS.¹⁸ Among these techniques, XRF suffers poor detection limits for REEs, which limit its application for REE detection in real samples. NAA is sensitive but requires access to a nuclear reactor, so it is not suitable for routine REE analysis. Although the IDMS assay allows fast and multielemental determination of REEs, the detection limit for REEs is still 2–3 orders of magnitude poorer

Received: December 6, 2011

Revised: March 5, 2012

Accepted: March 5, 2012

Published: March 5, 2012

than with ICP-MS. Relatively, ICP-MS is the most favorable choice, due to its excellent analytical performance such as high sensitivity and selectivity, part-per-trillion detection limit, wide linear range, and multielemental and multi-isotopic measurement capability without the problem of spectral interferences encountered in the ICP-AES assay. However, direct use of ICP-MS is considerably limited because its calibration range does not cover the concentration ranges of trace REEs, and various interferences occur in environmental, biological, and food samples. Therefore, preconcentration and separation procedures are necessary prior to determination.^{17,19–21}

A flow injection (FI) online microcolumn solid phase extraction (SPE) technique has attracted considerable practical interest for the separation and preconcentration of REEs,^{17,19–21} because of its advantages of high enrichment factor, rapid phase separation, and simple automated operation. It is worth noting that the adsorbent materials play a critical role in the FI online microcolumn SPE technique to improve the performance of the analytical method. Various materials, such as modified carbon nanomaterials,^{16,19} mesoporous titanium dioxide,²⁰ acetylaceton-modified silica gel,¹⁷ alkyl phosphonic acid resin,²¹ 8-quinolinole-immobilized fluorinated metal alkoxide glass,²² 2,6-diacetylpyridine functionalized Amberlite XAD-4,²³ maleic acid grafted polytetrafluoroethylene fibers,²⁴ and C₁₈-cartridge modified with PAN,²⁵ have been developed for the preconcentration of REEs. However, these adsorbent materials always need time-consuming and complicated modification of functional groups to improve their selectivity. It is extremely urgent to exploit some natural and easily available materials as adsorbent with high selectivity and high absorption capability. Many natural materials, such as activated carbons from leaves,²⁶ brown seaweeds,²⁷ fly ash,²⁸ green coconut shell powder,²⁹ lignocellulosic fibers,³⁰ spherical cellulose,³¹ peat moss,³² pine bark,³³ sugar beet pulp,³⁴ sawdust,³⁵ barley husk,³⁶ and bean coat,³⁷ have behaved as green adsorbents for the removal or preconcentration of trace heavy metals because these biosorbents are economical, easily available in the diet, nontoxic, and pollution free and have highly adsorption capacity. Another natural material, the walnut shell, has been studied and demonstrated to have good adsorption ability for various metals,^{38–41} although it is always abandoned in the routine diet. Owing to natural functional groups such as hydroxyl, carboxyl, carbonyl, and ester groups on the surface, the walnut shell has a strong potential for adsorption and preconcentration of heavy metals without the need of any complicated modification process.

In the present work, we report an online FI-SPE coupling to ICP-MS technique with the powdered walnut shell as a green adsorbent for the preconcentration and determination of REEs in food and agricultural products. The walnut shell packed microcolumn was validated to have a strong adsorption capacity and high interference-intolerance for REEs from complex matrices. Using the merits of walnut shell packed microcolumn and ICP-MS, high enrichment factor, large dynamic capacity, low detection limits, and high sample throughput were achieved. The accuracy and applicability of the developed online SPE technique was validated by analyzing REE contents in one certified rock reference material (GBW 07233) and three environmental certified reference materials (GBW 07310, GBW 10016, GBW 09101a). This work presents data from a preliminary study of REE levels in various food and agricultural products available on the Tianjin (China) market. Although the number of samples collected is limited, this study provides

information about REE content in routine food and agricultural products for the first time to our knowledge.

MATERIALS AND METHODS

Chemicals. The multi-REE stock solution containing Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu each at 100 mg L⁻¹ was purchased from the General Research Institute for Nonferrous Metals (Beijing, China). The intermediate multi-REE solution was prepared by diluting the original stock solution in 1% v/v HNO₃. Working multi-REE solutions were prepared by series dilution of the intermediate multi-REE solution immediately before use. Concentrated HNO₃ (65–68%, w/w), HCl (36–38%, w/w), and NH₃·H₂O (25–28%, w/w) solutions were of ultrapure grade (BV-III, Beijing Institute of Chemical Reagent, Beijing, China). All other reagents used were of the highest purity available but at least of analytical grade. Ultrapure water (18.2 MΩ cm) obtained from a WaterPro water system (Labconco Corp., Kansas City, MO, USA) was used throughout this work. All glassware and containers were soaked in acid solution (a mixture of one part concentrated HNO₃ with three parts water containing 1–2 drops of 30% H₂O₂) for at least a day and rinsed thoroughly with ultrapure water before use.

Apparatus. An X7 ICP-MS system equipped with a glass concentric nebulizer and PlasmaLab software (Thermo Elemental, Waltham, MA, USA) was used for the online simultaneous detection of REEs. The instrument was tuned daily to ensure consistent sensitivity, with standard tuning solution containing 1 μg L⁻¹ of Be, Co, In, and U (Multi-Element Tune D, Thermo Elemental, U.K.). The time-resolved analysis (TRA) mode (intensity vs time) was used to monitor the signals of the 15 REE ions. The peak area of a transient signal was used for quantification. PTFE tubing (20 cm long × 0.35 mm i.d.) was used to connect the injector of the FI system to the nebulizer of the ICP-MS instrument. The signal of ¹¹⁵In, added to the makeup solution at 1 μg L⁻¹ as internal standard, was monitored simultaneously and served to compensate for signal error. The experimental conditions of the ICP-MS system used throughout this work are listed in Table 1. An FIA-3100 FI system (Vital Instruments Co. Ltd., Beijing, China) was used to carry out the online preconcentration of trace rare earth elements. The FIA-3100 consists of two six-way peristaltic pumps and a standard two-rotary injection valve (eight ports on the rotor and eight ports on the stator). The FI online SPE operation sequence for the adsorption of REEs contained five steps, in which the pumped medium, flowing rate, valve position, duration time were well designed as shown in Figure S1 and Table S1 of the Supporting Information. Tygon pump tubes were employed to deliver the samples and reagents. Small-bore (0.35 mm i.d.) PTFE tubing was adapted for all connections, which were kept as short as possible to minimize the dead volume. The PTFE column (2 cm × 3 mm i.d.) packed with walnut shell powder was used for the online SPE.

Characterization of the Walnut Shell. To explore the potential adsorption mechanism of REEs onto the walnut shell, Fourier transform infrared (FT-IR) spectra of both the bare walnut shell and its derivative after adsorption and interaction of REEs (multi-REEs solution at pH 3.2 containing 15 REEs each at 1 mg L⁻¹) with the walnut shell were recorded using a IR200 spectrometer (Nicolet, USA), respectively. The morphologies and microstructures of the walnut shell were characterized by scanning electron microscope (SEM) on Shimadzu SS-550 (Kyoto, Japan) at 15.0 kV.

Preparation of the Walnut Shell Packed Microcolumn. The walnut (*Juglans regia*, origin of Hebei province, China) used in this work was purchased from the local supermarket (Tianjin, China). The walnut shell was collected after the edible nut had been procured and ground in a mortar with a pestle, and the ground powder was sieved to obtain a particle size between 0.2 and 0.5 mm. All of the walnut shell powder was washed thoroughly with distilled water and ultrapure water and then allowed to dry completely before column packing in a dust-free well-ventilated hood in a PTFE column with an effective length of 2 cm. The microcolumn was

Table 1. Instrumental Operation Conditions and Mass Spectrometer Settings for ICP-MS

parameter	setting
plasma	
RF power (W)	1192
cool gas flow rate (L min ⁻¹)	13.5
auxiliary gas flow rate (L min ⁻¹)	0.89
nebulizer gas flow rate (L min ⁻¹)	0.89
solution uptake rate (mL min ⁻¹)	1.2
mass spectrometer	
sampling cone	nickel, 1.1 mm orifice
skimmer cone	nickel, 0.75 mm orifice
analyzer vacuum (mbar)	4.1 × 10 ⁻⁷
resolution	normal
ion lenses	
extraction	-708
lens 1	-0.6
lens 2	-28.2
lens 3	-133.3
acquisition parameters	
measurement mode	profile TRA
dwelt time (ms)	1200
integration mode	peak area
detector	
PC detector	2854
analogue detector	1800
measured elements	
analytes	⁸⁹ Y; ¹³⁹ La; ¹⁴⁰ Ce; ¹⁴¹ Pr; ¹⁴⁶ Nd; ¹⁴⁷ Sm; ¹⁵¹ Eu; ¹⁵⁷ Gd; ¹⁵⁹ Tb; ¹⁶³ Dy; ¹⁶⁵ Ho; ¹⁶⁷ Er; ¹⁶⁹ Tm; ¹⁷⁴ Yb; ¹⁷⁵ Lu
internal standard	¹¹⁵ In

packed tightly with 0.1210 g walnut shell, blocked at both ends with glass wool, and then connected to the FI system by two end-screw connectors. Before use, the microcolumn was successively washed with distilled water, 10% aqua regia, and distilled water until no REE signal was detected by ICP-MS.

Samples and Sample Pretreatment. One rock certified reference material (CRM, GBW 07233, Institute of Geophysical and Geochemical Exploration, Langfang, China) and three environmental CRMs (GBW 07310 sediment, GBW 10016 tea leaves, GBW 09101a human hair, NRCMS, Beijing, China) were used to validate the accuracy of the developed online SPE method for detection of (ultra)trace REEs in real samples. Certified reference materials were prepared according to the literature with slight modification.¹⁹ Briefly, an accurately weighed sample portion of 0.1000 g was mixed with 3 mL of HNO₃ (65–68%, w/w) and 1 mL of H₂O₂ (30%, w/w) in a PTFE pressure vessel. The PTFE vessel was closed and left to stand overnight. The digestion vessels were then placed into a microwave oven. After that, the samples were digested in the microwave oven at 180 °C (ramp, 10 °C/min; hold, 15 min) with a power of 1.0 kW. After cooling, the vessels were opened and heated to near dryness on a hot plate at 200 °C. The residues were dissolved with 0.1 mol L⁻¹ HNO₃ and diluted to

100 mL with ultrapure water and adjusted to pH 3.2 with NH₃·H₂O and HNO₃. Proper dilution was further performed with ultrapure water and adjusted to pH 3.2 with NH₃·H₂O and HNO₃ immediately before analysis for samples containing high concentration of REEs. The blank was prepared exactly as the CRM samples.

All 18 food and agricultural samples (black fungus, tremella, kelp, laver, rice, brown rice, rape, long bean, cabbage, eggplant, potato, white gourd, dried mushroom, fresh bamboo shoot, red bean, corn, cayenne, garlic) were purchased from a local supermarket in Tianjin, China. The collected samples were rinsed with tap water, deionized water, and ultrapure water, three times respectively, and then dried and stored in clean vessels at room temperature for 12 h. Subsequently, about 100 g of each sample was ground into powder or milled into slurry. Aliquots of 0.5000 g for black fungus, tremella, kelp, laver, rape, long bean, cabbage, eggplant, potato, white gourd, dried mushroom, fresh bamboo shoot, cayenne, and garlic and 0.2500 g for rice, brown rice, red bean, and corn were accurately weighed and thoroughly mixed with 3 mL of HNO₃ (65–68%, w/w) and 1 mL of H₂O₂ (30%, w/w) in a Teflon vessel. Then the mixture was digested according to the same procedure as for the CRMs. Finally, the clear digest was transferred into a 100 mL calibrated flask and diluted to volume with ultrapure water. Diluted ammonia solution was used to adjust the final pH of the diluted digest to about 3.2. The digests of 18 food and agricultural samples were spiked with 15 REEs each at 2 ng L⁻¹ level to evaluate the recoveries. The blank solution was also prepared in parallel.

RESULTS AND DISCUSSION

Development of the Natural Walnut Shell as Green Adsorbent for Online Preconcentration of REEs. Walnut shell has a strong adsorption potential for heavy metals, owing to various functional groups such as hydroxyl, carboxyl, carbonyl, and ester groups on the surface.³⁷ Especially, the walnut shell can be directly used in online preconcentration for REEs without any complicated modification of the surface. In the present work, the powdered walnut shell was used as a green adsorbent for the preconcentration and determination of REEs in food and agricultural products. SEM images show clearly the shape and microstructures of the walnut shell powder (see Figure S2a-b of the Supporting Information). The abundant rough and porous structure should significantly increase the surface area of the walnut shell with natural functional groups, which increase obviously the adsorptive capacity of the walnut shell packed microcolumn as discussed later.

According to the published literature, the adsorption of heavy metals by bioadsorbent is mainly attributed to ion exchange,⁴² but electrostatic and coordinative interactions also exist.^{37,43} To validate the interactions existing between REE ions and the walnut shell, FT-IR spectra of the bare walnut shell before and after adsorption by REEs are shown in Figure 1. Spectral changes were observed at 3423 cm⁻¹ (the stretching vibration of O–H), 2922 cm⁻¹ (the asymmetric stretching vibration of C–H), 2361 cm⁻¹ (the peak of R–NH³⁺ groups), 1729 cm⁻¹ (the stretching vibration of C=O), 1631 cm⁻¹ (the asymmetric vibrations of –COO⁻), 1369 cm⁻¹ (the symmetric stretching vibrations of –COO⁻), 1240 cm⁻¹ (the stretching vibration of C–O in carboxylic acids), and 1058 cm⁻¹ (the stretching vibrations of C–O–C groups), respectively.^{44,45} Especially, the obvious peak red shifts occurred from 1729 and 1369 to 1740 and 1384 cm⁻¹, indicating that the electrostatic and coordinative interactions between the –COO⁻ group and REE ions may play a major role, because the empty π* orbit of –COO⁻ would receive the lone pair electrons of REE ions.^{37,46}

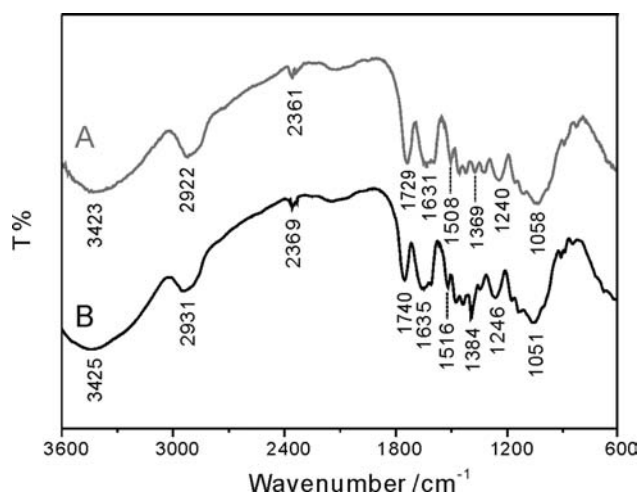


Figure 1. FT-IR spectra of (A) the bare walnut shell and (B) the derivative of walnut shell after adsorption by 15 REEs.

Besides, the peak at 1508 cm^{-1} showed the bending of N–H, which shifted to 1516 cm^{-1} after REE ion adsorption, where a coordinative bond might be formed and could be ascribed to lone electron pair donor of nitrogen atoms.⁴²

The dynamic capacity is an important parameter for the chosen sorbent in online application. The breakthrough capacity represents the exhaustion point in terms of feed volume, after which the absorbate leaks through into the effluent in gradually increasing amounts that can exceed the preset or desired value.^{47,48} The breakthrough capacity is calculated with the assumption that breakthrough occurs at $C_e/C_i = 0.01$,^{47,48} where C_e is the analyte concentration in the effluent and C_i is the analyte concentration in the influent. As shown in Figure S3 of the Supporting Information, the breakthrough capacity for 15 REE ions (each at 0.05 mg L^{-1} level, at pH 3.2) at a sample flow rate of 2.8 mL min^{-1} was calculated to be $24.8\text{ }\mu\text{g g}^{-1}$. The dynamic capacity is also an important parameter for the walnut shell sorbent in online application. On the basis of the reported procedure,^{24,47} the dynamic capacity of the powdered walnut shell was determined by passing multi-REEs solution at pH 3.2 containing 15 REE ions (each at 0.05 mg L^{-1} level) through the microcolumn packed with 0.1210 g of powdered walnut shell at a fixed flow rate until the concentration of the REE ions in the effluent was the same as in the influent online monitored by ICP-MS. The dynamic capacity of the walnut shell packed column was then determined as 0.41 mg g^{-1} of 15 REE ions. These results indicate that the walnut shells have potential for online SPE of REEs.

Selective Online SPE for REEs by Walnut Shell. To achieve good sensitivity and precision, the chemical and flow conditions were optimized for the FI online SPE for REEs coupled with ICP-MS. These variables include the pH of sample solution, selection of the eluent, sample loading time, and sample loading flow rate.

One of the critical variables for the adsorption of REEs on the sorbent surface is the sample acidity. When the sample solution is alkaline at $\text{pH} > 7$, REE ions would majorly be in the form of precipitate. Whereas the sample solution is too acid, the functional groups on the walnut shell are prone to be protonated and the positively charged walnut shell surface repulses the REE ions by electrostatic interaction.³⁷ The cases

above are both disadvantageous for the adsorption of REEs on the walnut shell packed column. Thus, the effect of sample acidity on the online SPE for REEs was studied in the range of pH 1.0–7.0 by preadjustment using diluted $\text{NH}_3\cdot\text{H}_2\text{O}$ and HNO_3 (see Figure 2 for Nd, Sm, Eu, Gd, Dy, Er, and Yb and

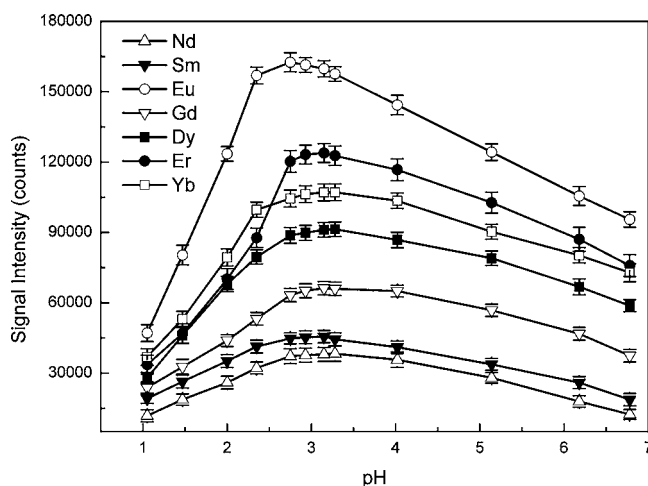


Figure 2. Influence of pH of the sample solution on the signal intensities of Nd, Sm, Eu, Gd, Dy, Er, and Yb each at 2.5 ng L^{-1} ($n = 3$). All other conditions were as in Figure S1 of the Supporting Information and Table 1.

Figure S4 of the Supporting Information for La, Y, Pr, Ce, Tb, Tm, Lu, and Ho). It can be seen that the signal intensity of 15 REEs increased with increasing pH of the solution up to 2.8 and leveled off until pH 3.4, but further increasing the pH resulted in obvious decrease of REE signal intensity. To maximize the extraction efficiency of 15 REE ions simultaneously, the sample solution was adjusted to pH 3.2 in the following experiments.

A suitable eluent also plays a critical role in the FI online preconcentration and determination system. It was found that H^+ competes with REE ions for the binding sites on the walnut shell. For this reason, an acid medium might be taken as eluent to desorb and elute the collected REE ions on the surface of walnut shell for the online ICP-MS detection. HNO_3 (in the concentration range of $0.75\text{--}3\text{ mol L}^{-1}$) or HCl (in the concentration range of $0.6\text{--}2.4\text{ mol L}^{-1}$) was independently investigated as the acid medium, but neither HNO_3 nor HCl could elute REEs from the walnut shell rapidly and completely. Finally, diluted aqua regia was chosen, and efficient elution was obtained. The effect of diluted aqua regia concentration on the desorption of REE ions was investigated in the range of 0.05–20% as shown in Figure 3. Obviously, 10% aqua regia was enough to achieve efficient elution of REEs and thus was used as the eluent throughout the further experiment. The flow rate of 10% aqua regia for elution was optimized from 1.6 to 2.8 mL min^{-1} in light of sensitivity and precision; 2.0 mL min^{-1} was selected for elution to ensure good precision and to obtain reasonable sensitivity.

The effects of sample loading time and sample flow rate on the FI online SPE of REEs were then investigated as shown in Figure 4 for Nd, Sm, Eu, Gd, Dy, Er, and Yb and in Figure S5a–b of the Supporting Information for La, Y, Pr, Ce, Tb, Tm, Lu, and Ho. It was found that the signal intensity of 15 REEs increased almost linearly as sample loading time increased up to

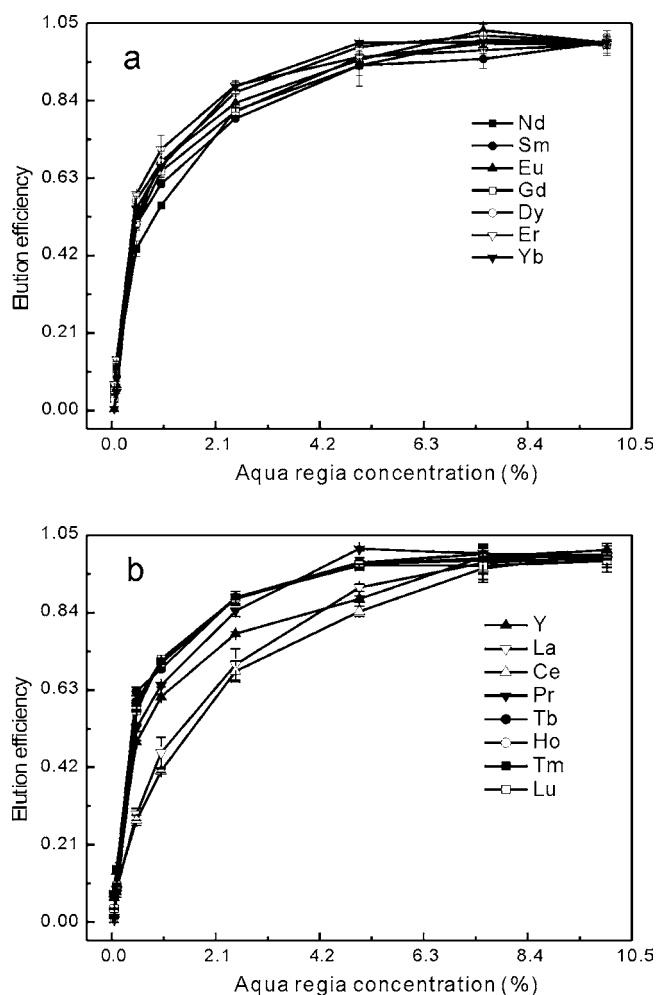


Figure 3. Effect of the concentration of diluted aqua regia as eluent on the elution efficiencies of 15 REE ions at 2.5 ng L^{-1} ($n = 3$). All other conditions were as in Figure S1 of the Supporting Information and Table 1.

220 s. Study on the effect of sample loading flow rate on the online SPE of 15 REEs at 2.5 ng L^{-1} for 100 s showed that the signal intensity increased linearly with the sample loading flow rate increasing up to 4.2 mL min^{-1} . The wide range of linearity for signal intensity against sample loading time and flow rate offered great potentiality for achieving high enhancement factors and high sensitivity by increasing sample loading rates and sample loading time without losing extraction efficiency. For the further work, a sample loading time of 100 s and a flow rate of 2.8 mL min^{-1} were selected for 15 REEs as a compromise of sensitivity and sample throughput.

Under the optimized conditions, the 15 REE signal intensities obtained by walnut shell packed microcolumn preconcentration were compared with those obtained without preconcentration as shown in Figure 5 for Nd, Sm, Eu, Gd, Dy, Er, and Yb and in Figure S6 of the Supporting Information for La, Y, Pr, Ce, Tb, Tm, Lu, and Ho. Taking Eu and Lu as examples, the signal intensities present 62- and 101-fold increases using our FI-ICP-MS analysis method in comparison with those obtained without preconcentration as shown in the insets of Figure 5 and Figure S6 of the Supporting Information, respectively. Accordingly, the REEs could be efficiently preconcentrated using walnut shell as the absorbent, and their signal intensities were thus magnified to give powerful

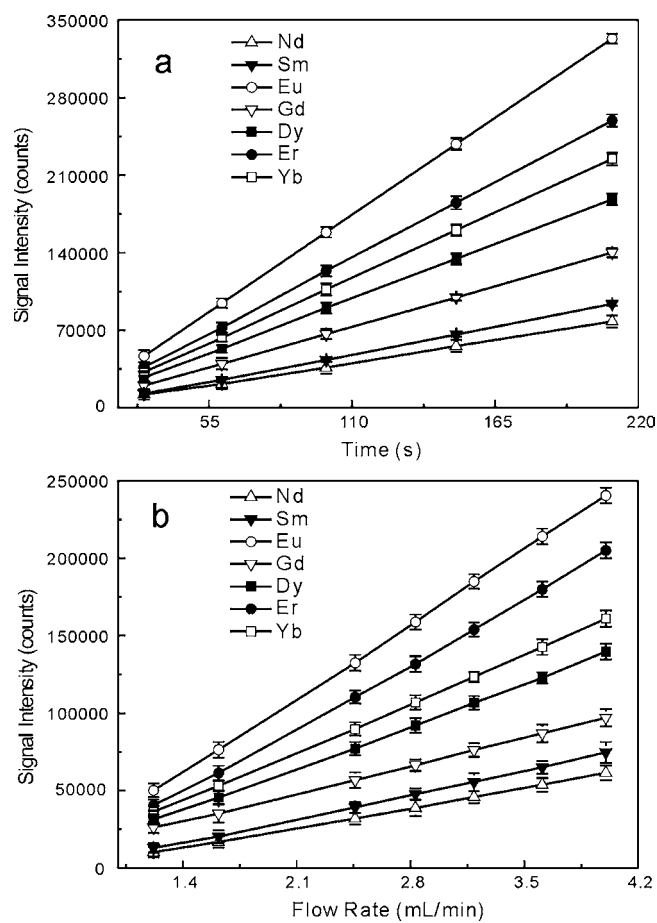


Figure 4. Effect of the sample loading time (a) and sample flow rate (b) on the signal intensities of Nd, Sm, Eu, Gd, Dy, Er, and Yb each at 2.5 ng L^{-1} ($n = 3$). All other conditions were as in Figure S1 of the Supporting Information and Table 1.

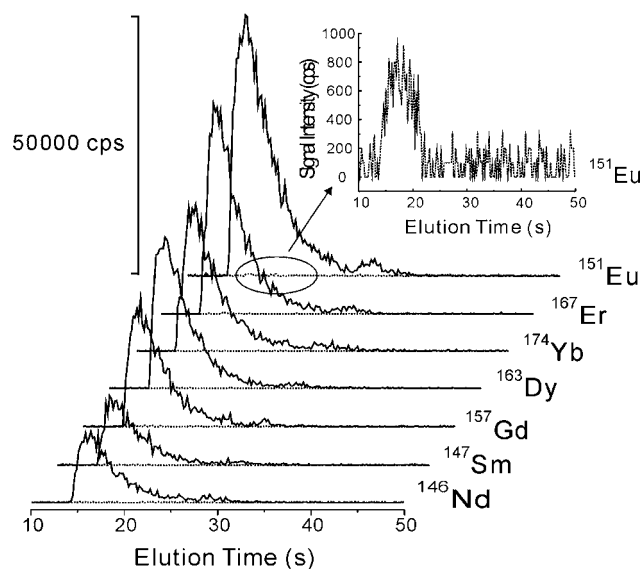


Figure 5. Comparison of the signals recorded by ICP-MS with preconcentration (in solid lines) and without preconcentration (in dot lines) by the walnut shell packed microcolumn for Nd, Sm, Eu, Gd, Dy, Er, and Yb each at the same concentration of 10 ng L^{-1} . (Inset) Signal of Eu magnified by change of the y-axis dimension without preconcentration by the walnut shell packed microcolumn.

enhancement factors of the developed method as discussed later.

The selectivity of the walnut shell for online SPE of REEs was tested because this method was applied for REE determination in the real biological and environmental sample with complicated matrices. To achieve this purpose, the effect of coexisting ions on the recovery of multi-REE solution containing 15 REE metals each at 12.5 ng L^{-1} level was studied under the optimized conditions as summarized in Table 2. The

Table 2. Effect of Coexisting Ions on Determination of REEs in Standard Solution at the 12.5 ng L^{-1} Level

coexisting ion	concentration ratio ^a
NO_3^- , CO_3^{2-} , SO_4^{2-} , H_2PO_4^- , SiO_3^{2-} , Cl^- , Br^- , I^-	80 000 000
NH_4^+ , Na^+ , Mg^{2+} , Sr^{2+}	40 000 000
K^+ , Ba^{2+b}	8 000 000
Cu^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Cd^{2+} , Ca^{2+}	4 000 000
Hg^{2+} , Co^{2+} , Cr^{3+} , Zn^{2+} , Ag^+ , $\text{B}_4\text{O}_7^{2-}$, Ti^{4+} , VO_3^-	2 000 000
Sn^{2+} , SeO_3^{2-} , Pb^{2+} , Fe^{2+}	1 500 000
AsO_3^{3-} , Bi^{3+}	600 000
$\text{H}_2\text{Sb}_2\text{O}_7^{2-}$	100 000
Al^{3+}	40 000
Ba^{2+c}	2 000

^aConcentration ratio = foreign ion/REE³⁺; the concentration of each foreign ion is the maximum amount tested. ^bThe tolerance limit of Ba^{2+} to REE³⁺, except Eu^{3+} . ^cThe tolerance limit of Ba^{2+} to Eu^{3+} .

tolerance limit of coexisting ions is defined as the largest amount making the recovery of the analyte no less than 90%. It is obvious that the developed method has a powerful tolerance capacity to interference from coexisting ions for preconcentration and determination of REEs. The results showed that up to 4–8 orders of magnitude of concentration ratios for the coexisting ions to REE ions ensure no interference to the determination of REEs by the walnut shell packed microcolumn SPE. Generally, the contents of coexisting ions in real samples after digestion or appropriate dilution will not exceed the tolerant concentration levels studied in this work; therefore, the present procedure can be applied for the determination of trace REE ions in real samples without the use of complex pretreatment or masking reagent. Certainly as demonstrated

later, the present online SPE system allowed the interference-free extraction of ultratrace REEs in the environmental, food, and agricultural products studied.

Figures of Merit for the Present FI Online Walnut Shell Packed Microcolumn Preconcentration and Determination of REEs with ICP-MS. The analytical figures of merit of the present online SPE using walnut shell packed microcolumn coupled with ICP-MS for the determination of trace REEs were evaluated under optimal experimental conditions as shown in Table 3. With a sample loading volume of 4.7 mL, the enrichment factors (EF) obtained by comparing the slopes of the linear portion of the calibration curves before and after the preconcentration were in the range of 79–102. The detection limits, defined as the concentration of the analytes corresponding to 3 times the standard deviation (3s) for 11 replicate detections of the procedural blanks, were in the range of 2–34 pg g^{-1} . The quantification limits, defined as the concentration of the analytes corresponding to 10 times the standard deviation (10s) for 11 replicate detections of the procedural blanks, were in the range of 6–113 pg g^{-1} . The sample throughput of the developed method was about 23 samples h^{-1} , and the precision expressed as the relative standard deviation (RSD) for 11 replicate determinations of the 15 REEs at the 2.5 ng L^{-1} level ranged from 0.5 to 2.0%. The day-to-day reproducibility of the present FI online walnut shell packed microcolumn preconcentration and determination of REEs with ICP-MS was obtained in the range of 2.4–5.0% for sequential 5 day determinations of the 15 REEs at the 2.5 ng L^{-1} level.

The stability of the microcolumn with walnut shell as adsorbent was then investigated for online preconcentration and determination of REEs. The extraction efficiency of the walnut shell packed microcolumn for REE ions was not changed even after 1000 successive cycles of preconcentration/elution procedure and online ICP-MS detections, indicating good stability of the developed online preconcentration system with walnut shell as sorbent coupled with ICP-MS during 47 h of running. The advantage of long stability may be ascribed to the characteristic of stiff texture and small swelling coefficient of walnut shell, as well as the efficient elution using 10% aqua regia as eluent.

Table 3. Characteristic Data for the Online Walnut Shell Packed Microcolumn SPE Coupled with ICP-MS for Detection of Trace REEs

isotope	enhancement factor	precision ($n = 11$, 2.5 ng L^{-1}) (%)	detection limit (3s) ($\text{pg g}^{-1}/\text{ng L}^{-1}$)	quantification limit (10s) ($\text{pg g}^{-1}/\text{ng L}^{-1}$)	linear range (ng L^{-1})	correlation coefficient
⁸⁹ Y	79	1.5	8/0.04	26/0.13	0.25–1250	0.9996
¹³⁹ La	80	1.1	34/0.17	113/0.57	0.75–1250	0.9999
¹⁴⁰ Ce	82	1.3	32/0.16	106/0.53	0.75–1250	0.9999
¹⁴¹ Pr	85	1.1	6/0.03	20/0.10	0.25–1250	0.9997
¹⁴⁵ Nd	81	0.8	26/0.13	86/0.43	0.50–1250	0.9998
¹⁴⁷ Sm	81	1.0	18/0.09	60/0.30	0.50–1250	0.9995
¹⁵¹ Eu	80	2.0	8/0.04	26/0.13	0.50–1250	0.9999
¹⁵⁷ Gd	84	2.0	16/0.08	53/0.27	0.50–1250	0.9997
¹⁵⁹ Tb	89	1.4	4/0.02	13/0.07	0.10–1250	0.9998
¹⁶¹ Dy	79	1.5	8/0.04	26/0.13	0.25–1250	0.9998
¹⁶⁵ Ho	84	0.8	2/0.01	6/0.03	0.10–1250	0.9999
¹⁶⁶ Er	83	0.9	4/0.02	13/0.07	0.25–1250	0.9998
¹⁶⁹ Tm	102	0.5	2/0.01	6/0.03	0.10–1250	0.9999
¹⁷² Yb	88	0.8	14/0.07	46/0.23	0.25–1250	0.9999
¹⁷⁵ Lu	96	1.4	4/0.02	13/0.07	0.10–1250	0.9999

Table 4. Analytical Results (Mean \pm s, $n = 3$) of the Trace REEs Contents in Certified Reference Materials

element	concentration ($\mu\text{g g}^{-1}$)				concentration (ng g^{-1})			
	GBW 07310 sediment		GBW 07233 copper ore		GBW 10016 tea leaf		GBW 09101a human hair	
	certified	determined	certified	determined	certified	determined	certified	determined
Y	14 \pm 3	12 \pm 1	7.3 \pm 0.5	7.5 \pm 0.2	230 \pm 30	220 \pm 20	7.5 ^a	8.4 \pm 0.9
La	13 \pm 1.4	12 \pm 0.5	7.5 \pm 0.4	7.8 \pm 0.3	250 \pm 20	240 \pm 30	13.4 \pm 1.8	14.1 \pm 0.9
Ce	58 \pm 5	57 \pm 1	13.2 \pm 1.4	14.1 \pm 0.5	390 \pm 50	381 \pm 45	19.7 \pm 2.6	17.3 \pm 2.0
Pr	3.2 \pm 0.4	3.0 \pm 0.2	1.4 \pm 0.2	1.5 \pm 0.5	42 \pm 4	40 \pm 3	2.4 ^a	2.2 \pm 0.3
Nd	11.8 \pm 1.6	12.5 \pm 0.5	4.7 \pm 0.1	4.6 \pm 0.2	150 \pm 20	148 \pm 20	8.4 \pm 1.6	8.0 \pm 1.5
Sm	2.4 \pm 0.2	2.5 \pm 0.1	1.0 \pm 0.2	1.1 \pm 0.1	29 \pm 3	30 \pm 2	1.4 \pm 0.4	1.5 \pm 0.4
Eu	0.47 \pm 0.05	0.49 \pm 0.02	0.28 \pm 0.03	0.30 \pm 0.02	6.7 \pm 1.4	6.8 \pm 0.8	0.6 ^a	0.7 \pm 0.1
Gd	2.2 \pm 0.3	2.0 \pm 0.1	1.1 \pm 0.2	1.2 \pm 0.2	31 \pm 5	30 \pm 4	1.8 ^a	1.6 \pm 0.2
Tb	0.42 \pm 0.11	0.45 \pm 0.07	0.21 \pm 0.05	0.22 \pm 0.02	4.5 \pm 0.7	4.6 \pm 0.5	0.2 ^a	0.2 \pm 0.01
Dy	2.2 \pm 0.3	2.0 \pm 0.02	1.1 \pm 0.2	1.2 \pm 0.1	25 \pm 6	25 \pm 3	1.3 ^a	1.4 \pm 0.3
Ho	0.45 \pm 0.08	0.50 \pm 0.02	0.26 \pm 0.03	0.28 \pm 0.02	5.4 \pm 1.2	5.5 \pm 0.9	0.3 ^a	0.2 \pm 0.01
Er	1.3 \pm 0.2	1.3 \pm 0.1	0.78 \pm 0.10	0.80 \pm 0.03	14 \pm 4	15 \pm 2	0.7 ^a	0.5 \pm 0.02
Tm	0.20 \pm 0.04	0.19 \pm 0.02	0.11 \pm 0.03	0.10 \pm 0.03	2.6 \pm 1.0	2.5 \pm 0.7	0.1 ^a	0.1 \pm 0.01
Yb	1.2 \pm 0.3	1.3 \pm 0.1	0.89 \pm 0.06	0.91 \pm 0.02	18 \pm 4	16 \pm 5	0.8 ^a	0.9 \pm 0.02
Lu	0.19 \pm 0.04	0.20 \pm 0.02	0.16 \pm 0.03	0.15 \pm 0.01	3.0 \pm 0.8	2.8 \pm 0.6	0.2 ^a	0.2 \pm 0.01

^aNo standard deviations were available for these certified concentrations.

Validation and Application of the Developed FI Online Preconcentration and Determination of REEs with ICP-MS in Food and Agricultural Products. To validate the analytical reliability of the developed online SPE technique for REEs, one certified rock reference material (GBW 07233) and three environmental certified reference materials (GBW 07310, GBW 10016, GBW 09101a) were analyzed. The analytical results by the present method using simple aqueous standards for calibration are given in Table 4. The determined concentrations of REEs agreed well with the certified values at a confidence level of 90 or 95%, as corroborated by a *t* test, despite the high contents of potential interfering elements in these samples (Table S3 of the Supporting Information, except that no content of coexisting elements is available for GBW 09101a).

To further evaluate the applicability of the developed method, the species and concentrations of trace REEs were determined in 18 agricultural and food samples in Tianjin, China, as shown in Table 5 and Tables S4 and S5 of the Supporting Information, respectively. The recoveries of REEs at the 2 ng L⁻¹ level spiked in the digests of these food and agricultural products ranged from 89 to 105%, indicating no or little interference encountered from the complex matrices. By comparison of the determined species and various REE concentrations in different food and agricultural products, it is not difficult to find the following sequence: oceanic products (such as kelp, laver) > rootstock generic products (such as garlic, potato, dried mushroom, fresh bamboo shoot, black fungus, tremella, rape, cabbage) > fruit generic products (such as rice, white gourd, brown rice, long bean, eggplant, red bean, corn, cayenne) not only as of the detected species of rare earth element but also the REE concentration. The light REE (LREEs, from La to Gd) content is significantly higher than that of heavy REEs (HREEs, from Tb to Lu) for each real sample. Generally, agricultural fertilizer and industrial drainage would result in higher REE concentration in the farmland. Therefore, the rootstock generic food and agricultural products grown in the soil were detected with higher concentration of REEs

than those fruit generic products. The relatively high content of REEs (such as Y, La, Ce, Nd, Sm, Gd, and Dy) determined in oceanic products might be ascribed to REE accumulation in the ocean with the natural air and water circulation.

Comparison of the Developed FI Online Preconcentration and Determination of REEs with ICP-MS with Other Techniques. Comprehensive consideration of the developed method with other methods for the preconcentration and determination of REEs is shown in Table S2 of the Supporting Information. The detection limits of 15 REEs obtained by the present method are 2–5 orders of magnitude lower than those obtained by ICP-AES,¹⁶ FI-ICP-AES,¹⁷ FI-MPT-AES,⁴⁹ FI-ICP-MS,¹⁹ ICP-MS,²³ and FI-ICP-OES²⁵ and similar to those obtained by FI-ICP-OES,²⁰ FI-ICP-MS,^{21,22,24} and FI-ICP-TOFMS.⁵⁰ It is obvious that the present method has a higher or similar enrichment factor but with less sample volume and higher sampling throughput than other methods. Especially, due to the stiff texture and small swelling coefficient of the walnut shell, the as-prepared microcolumn has a long lifetime for more than 1000 usages. Compared with other materials, the walnut shell is a kind of natural, green, and safe adsorbent without any complicated modification with functional groups.

In summary, a practical SPE using a walnut shell packed microcolumn was developed to separate and preconcentrate trace REEs in environmental, biological, and food samples prior to determination by ICP-MS. Compared with other methods, the present FI-SPE-ICP-MS technique was demonstrated to have advantages of higher enrichment factor and powerful tolerance to complex coexisting matrices. The feasibility and reliability of the method was well validated by analyzing REE content in different environmental and biological certified reference materials, and this method has been applied for the REE determination in various food and agricultural products available on the local market.

Table 5. Analytical Results (Mean \pm s, n = 3) of the Trace REE Contents in Agricultural and Food Products

element	concentration (ng g ⁻¹)												rice recovery				
	lavender			kelp			potato			black fungus				eggplant			
	determined	recovery		determined	recovery		determined	recovery		determined	recovery			determined	recovery		
Y	179.6 \pm 1.2	101		126.5 \pm 0.9	102		11.0 \pm 0.06	97		11.6 \pm 0.2	89		1.3 \pm 0.01	102		nd ^a	96
La	54.0 \pm 0.8	99		59.8 \pm 0.5	101		17.7 \pm 0.2	96		17.6 \pm 0.1	94		1.9 \pm 0.02	90		1.5 \pm 0.01	95
Ce	55.1 \pm 0.9	95		85.0 \pm 0.7	91		38.9 \pm 0.3	96		67.7 \pm 0.8	92		7.2 \pm 0.08	93		nd	94
Pr	26.6 \pm 0.2	97		17.5 \pm 0.1	98		7.6 \pm 0.1	105		4.5 \pm 0.1	102		0.3 \pm 0.01	92		nd	95
Nd	46.5 \pm 0.6	95		56.5 \pm 0.5	97		15.6 \pm 0.2	91		38.9 \pm 0.5	105		1.2 \pm 0.06	98		nd	96
Sm	36.3 \pm 0.4	95		11.9 \pm 0.1	92		8.8 \pm 0.1	90		5.7 \pm 0.1	98		1.4 \pm 0.03	94		nd	94
Eu	6.6 \pm 0.09	99		2.1 \pm 0.02	92		1.8 \pm 0.06	92		0.5 \pm 0.04	95		nd	96		nd	91
Gd	19.5 \pm 0.1	96		13.6 \pm 0.1	96		7.2 \pm 0.1	97		3.9 \pm 0.2	95		0.1 \pm 0.01	95		nd	90
Tb	3.5 \pm 0.02	93		2.3 \pm 0.03	95		1.0 \pm 0.01	96		0.2 \pm 0.02	103		nd	95		nd	92
Dy	68.7 \pm 0.9	92		13.9 \pm 0.08	94		2.9 \pm 0.02	102		4.6 \pm 0.1	91		1.0 \pm 0.02	96		nd	91
Ho	30.6 \pm 0.5	90		3.0 \pm 0.05	95		0.8 \pm 0.01	91		0.6 \pm 0.02	92		nd	91		nd	91
Er	2.4 \pm 0.03	98		10.4 \pm 0.06	93		2.2 \pm 0.04	90		1.6 \pm 0.2	96		0.3 \pm 0.02	90		nd	90
Tm	10.0 \pm 0.07	104		1.6 \pm 0.02	97		0.2 \pm 0.01	98		0.1 \pm 0.02	93		0.5 \pm 0.03	104		nd	95
Yb	5.9 \pm 0.01	90		11.1 \pm 0.1	96		1.9 \pm 0.02	99		1.4 \pm 0.1	97		nd	97		nd	93
Lu	7.6 \pm 0.02	92		2.0 \pm 0.03	105		0.2 \pm 0.01	96		0.1 \pm 0.02	99		nd	95		nd	103

^and, not detectable.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +86-22-23503034. E-mail: nkliyan398@gmail.com.

Funding

Financial support from the National Natural Science Foundation of China (20975054), the Key Project of Chinese Ministry of Education (109040), the Fok Ying Tong Education Foundation (114041), the Program for New Century Excellent Talents (NCET-09-0482), the Foundation for the Author of National Excellent Doctoral Dissertation of People's Republic of China (FANEDD-201023), and the Foundation for Bohai Scholar of Tianjin Normal University (SRL098 and SRL106) is gratefully acknowledged.

Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Von Tucher, S.; Goy, C.; Schmidhalter, U. Effect of lanthanum on growth and composition of mineral nutrients of *Phaseolus vulgaris* L. var. *nanus* and *Zea mays* L. conv. *Saccharata*. In *Plant Nutrition – Food Security and Sustainability of Agro-ecosystems*; Horst, W. J. et al., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001; pp 524–525.
- (2) Buckingham, S.; Maheswaran, J.; Meehan, B.; Peverill, K. The role of applications of rare earth elements in enhancement of crop and pasture production. *Mater. Sci. Forum* **1999**, *315*, 339–347.
- (3) Zhu, H. D.; Wu, Q.; Fan, T. J.; Liu, Q. F.; Zhang, W. Elemental transfer from Chinese soil via the diet to the whole human body. *J. Radiol. Prot.* **2008**, *28*, 573–580.
- (4) Hirano, S.; Suzuki, K. T. Exposure, metabolism, and toxicity of rare earths and related compounds. *Environ. Health Perspect.* **1996**, *104*, 85–95.
- (5) Chen, Z. Y.; Zhu, X. D. Accumulation of rare earth elements in bone and its toxicity and potential hazard to health. *J. Ecol. Rural Environ.* **2008**, *24*, 88–91.
- (6) Aniwashi, J.; Kaleri, H. A.; Sulaiman, Y.; Qi-fa, L.; Zhuang, X. Interactions between rare-earth ions and DNA of Bashibai sheep. *Genet. Mol. Res.* **2011**, *10*, 1075–1083.
- (7) Zhu, W. F.; Xu, S. Q.; Shao, P. P.; Zhang, H.; Wu, D. S.; Yang, W. J.; Feng, J. Bioelectrical activity of the central nervous system among populations in a rare earth element area. *Biol. Trace Elem. Res.* **1997**, *57*, 71–77.
- (8) Chang, C. W.; Qu, B.; Hong, Z.; Gao, G. D. Potentiation of inhibitory amino acid receptors-mediated responses by lanthanum in rat sacral dorsal commissural neurons. *Neurotoxicol. Teratol.* **2006**, *28*, 657–663.
- (9) Highsmith, S. R.; Head, M. R. Tb³⁺ binding to Ca²⁺ and Mg²⁺ binding sites on sarcoplasmic reticulum ATPase. *J. Biol. Chem.* **1983**, *258*, 6858–6862.
- (10) Liu, Y.; Chen, Z. Y.; Wang, Y. X. Distribution and accumulation of neodymium and its effect on secretion of progesterone in mice. *J. Rare Earths* **2004**, *22*, 292–295.
- (11) Haley, T. J.; Raymond, K.; Komesu, N.; Upham, H. C. Toxicological and pharmacological effects of gadolinium and samarium chlorides. *Brit. J. Pharmacol.* **1961**, *17*, 526–532.
- (12) Orvini, E.; Speziali, M.; Salvini, A.; Herborg, C. Rare earth elements determination in environmental matrices by INAA. *Microchem. J.* **2000**, *67*, 97–104.
- (13) De Vito, I. E.; Olsina, R. A.; Masi, A. N. Preconcentration and elimination of matrix effects in XRF determinations of rare earth

elements by preparing a thin film through chemofiltration. *J. Anal. At. Spectrom.* **2001**, *16*, 275–278.

(14) Shaw, T. J.; Duncan, T.; Schnetger, B. A preconcentration/matrix reduction method for the analysis of rare earth elements in seawater and groundwaters by isotope dilution ICPMS. *Anal. Chem.* **2003**, *75*, 3396–3403.

(15) Pascinli, T.; Eroğlu, A. E.; Shahwan, T. Preconcentration and atomic spectrometric determination of rare earth elements (REEs) in natural water samples by inductively coupled plasma atomic emission spectrometry. *Anal. Chim. Acta* **2005**, *547*, 42–49.

(16) Liang, P.; Liu, Y.; Guo, L. Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry after preconcentration with multiwalled carbon nanotubes. *Spectrochim. Acta, Part B* **2005**, *60*, 125–129.

(17) Zhang, N.; Huang, C. Z.; Hu, B. ICP-AES determination of trace rare earth elements in environmental and food samples by on-line separation and preconcentration with acetylaceton-modified silica gel using microcolumn. *Anal. Sci.* **2007**, *23*, 997–1002.

(18) Spalla, S.; Baffi, C.; Barbante, C.; Turretta, C.; Cozzi, G.; Beone, G. M.; Bettinelli, M. Determination of rare earth elements in tomato plants by inductively coupled plasma mass spectrometry techniques. *Rapid Commun. Mass Spectrom.* **2009**, *23*, 3285–3292.

(19) Chen, S. Z.; Xiao, M. F.; Lu, D. B.; Zhan, X. L. Use of a microcolumn packed with modified carbon nanofibers coupled with inductively coupled plasma mass spectrometry for simultaneous on-line preconcentration and determination of trace rare earth elements in biological samples. *Rapid Commun. Mass Spectrom.* **2007**, *21*, 2524–2528.

(20) Huang, C. Z.; Jiang, Z. C.; Hu, B. Mesoporous titanium dioxide as a novel solid-phase extraction material for flow injection micro-column preconcentration on-line coupled with ICP-OES determination of trace metals in environmental samples. *Talanta* **2007**, *73*, 274–281.

(21) Fu, Q.; Yang, L. M.; Wang, Q. Q. On-line preconcentration with a novel alkyl phosphonic acid extraction resin coupled with inductively coupled plasma mass spectrometry for determination of trace rare earth elements in seawater. *Talanta* **2007**, *72*, 1248–1254.

(22) Kajiyu, T.; Aihara, M.; Hirata, S. Determination of rare earth elements in seawater by inductively coupled plasma mass spectrometry with on-line column pre-concentration using 8-quinolinole-immobilized fluorinated metal alkoxide glass. *Spectrochim. Acta, Part B* **2004**, *59*, 543–550.

(23) Karadaş, C.; Kara, D.; Fisher, A. Determination of rare earth elements in seawater by inductively coupled plasma mass spectrometry with off-line column preconcentration using 2,6-diacetylpyridine functionalized Amberlite XAD-4. *Anal. Chim. Acta* **2011**, *689*, 184–189.

(24) Wang, Z. H.; Yan, X. P.; Wang, Z. P.; Zhang, Z. P.; Liu, L. W. Flow injection on-line solid phase extraction coupled with inductively coupled plasma mass spectrometry for determination of (ultra)trace rare earth elements in environmental materials using maleic acid grafted polytetrafluoroethylene fibers as sorbent. *J. Am. Soc. Mass Spectrom.* **2006**, *17*, 1258–1264.

(25) Bahramifar, N.; Yamini, Y. On-line preconcentration of some rare earth elements in water samples using C₁₈-cartridge modified with 1-(2-pyridylazo) 2-naphthol (PAN) prior to simultaneous determination by inductively coupled plasma optical emission spectrometry (ICP-OES). *Anal. Chim. Acta* **2005**, *540*, 325–332.

(26) Ranganathan, K. Chromium removal by activated carbons prepared from *Casurina equisetifolia* leaves. *Bioresour. Technol.* **2000**, *73*, 99–103.

(27) Figueira, M. M.; Volesky, B.; Ciminelli, V. S. T.; Roddick, F. A. Biosorption of metals in brown seaweed biomass. *Water Res.* **2000**, *34*, 196–204.

(28) Pehlivan, E.; Cetin, S.; Yanik, B. H. Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash. *J. Hazard. Mater.* **2006**, *B135*, 193–199.

(29) Pino, G. H.; De Mesquita, L. M. S.; Torem, M. L.; Pinto, G. A. S. Biosorption of cadmium by green coconut shell powder. *Miner. Eng.* **2006**, *19*, 380–387.

(30) Lee, B. G.; Rowell, R. M. Removal of heavy metal ions from aqueous solutions using lignocellulosic fibers. *J. Nat. Fibers* **2004**, *1*, 97–108.

(31) Liu, M. H.; Deng, Y.; Zhan, H. Y.; Zhan, X. S. Adsorption and desorption of copper(II) from solutions on new spherical cellulose adsorbent. *J. Appl. Polym. Sci.* **2002**, *84*, 478–485.

(32) Crist, R. H.; Martin, J. R.; Chonko, J.; Crist, D. R. Uptake of metals on peat moss: an ion-exchange process. *Environ. Sci. Technol.* **1996**, *30*, 2456–2461.

(33) Al-Asheh, S.; Duvnjak, Z. Sorption of cadmium and other heavy metals by pine bark. *J. Hazard. Mater.* **1997**, *56*, 35–51.

(34) Reddad, Z.; Gerente, C.; Andres, Y.; Le Cloirec, P. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.* **2002**, *36*, 2067–2073.

(35) Yu, B.; Zhang, Y.; Shukla, A.; Shukla, S. S.; Dorris, K. L. The removal of heavy metals from aqueous solutions by sawdust adsorption-removal of lead and comparison of its adsorption with copper. *J. Hazard. Mater.* **2001**, *B84*, 83–94.

(36) Robinson, T.; Chandran, B.; Naidu, G. S.; Nigam, P. Studies on the removal of dyes from a synthetic textile effluent using barley husk in static-batch mode and in a continuous flow, packed-bed, reactor. *Bioresour. Technol.* **2002**, *85*, 43–49.

(37) Tian, Y.; Xie, Z. M.; Chen, M. L.; Wang, J. H. Cadmium preconcentration with bean-coat as a green adsorbent with detection by electrothermal atomic absorption spectrometry. *J. Anal. At. Spectrom.* **2011**, *26*, 1408–1413.

(38) Ahmedna, M.; Marshall, W. E.; Husseiny, A. A.; Rao, R. M.; Goktepe, I. The use of nutshell carbons in drinking water filters for removal of trace metals. *Water Res.* **2004**, *38*, 1062–1068.

(39) Altun, T.; Pehlivan, E. Removal of copper(II) ions from aqueous solutions by walnut-, hazelnut- and almond-shells. *Clean* **2007**, *35*, 601–606.

(40) Pehlivan, E.; Altun, T. Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell. *J. Hazard. Mater.* **2008**, *155*, 378–384.

(41) Zabihi, M.; Ahmadpour, A.; Asl, A. H. Removal of mercury from water by carbonaceous sorbents derived from walnut shell. *J. Hazard. Mater.* **2009**, *167*, 230–236.

(42) Saeed, A.; Iqbal, M.; Höll, W. H. Kinetics, equilibrium and mechanism of Cd²⁺ removal from aqueous solution by mungbean husk. *J. Hazard. Mater.* **2009**, *168*, 1467–1475.

(43) Iqbal, M.; Saeed, A.; Zafar, S. I. FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd²⁺ and Pb²⁺ removal by mango peel waste. *J. Hazard. Mater.* **2009**, *164*, 161–171.

(44) Farinella, N. V.; Matos, G. D.; Arruda, M. A. Z. Grape bagasse as a potential biosorbent of metals in effluent treatments. *Bioresour. Technol.* **2007**, *98*, 1940–1946.

(45) Ofomaja, A. E.; Ho, Y. S. Effect of pH on cadmium biosorption by coconut copra meal. *J. Hazard. Mater.* **2007**, *B139*, 356–362.

(46) Wells, M.; Dermody, D. L.; Yang, H. C.; Kim, T.; Crooks, R. M. Interactions between organized, surface-confined monolayers and vapor-phase probe molecules. 9. Structure/reactivity relationship between three surface-confined isomers of mercaptobenzoic acid and vapor-phase decylamine. *Langmuir* **1996**, *12*, 1989–1996.

(47) Wang, X. R.; Barnes, R. M. Chelating resins for on-line flow injection pre-concentration with inductively coupled plasma atomic emission spectrometry. *J. Anal. At. Spectrom.* **1989**, *4*, 509–518.

(48) Fang, G. Z.; Tan, J.; Yan, X. P. An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol-gel process for selective solid-phase extraction of cadmium(II). *Anal. Chem.* **2005**, *77*, 1734–1739.

(49) Jia, Q.; Kong, X. F.; Zhou, W. H.; Bi, L. H. Flow injection on-line preconcentration with an ion-exchange resin coupled with microwave plasma torch-atomic emission spectrometry for the determination of trace rare earth elements. *Microchem. J.* **2008**, *89*, 82–87.

(50) Benkhedda, K.; Infante, H. G.; Ivanova, E.; Adams, F. C. Determination of sub-parts-per-trillion levels of rare earth elements in natural waters by inductively coupled plasma time-of-flight mass spectrometry after flow injection on-line sorption preconcentration in a knotted reactor. *J. Anal. At. Spectrom.* **2001**, *16*, 995–1001.