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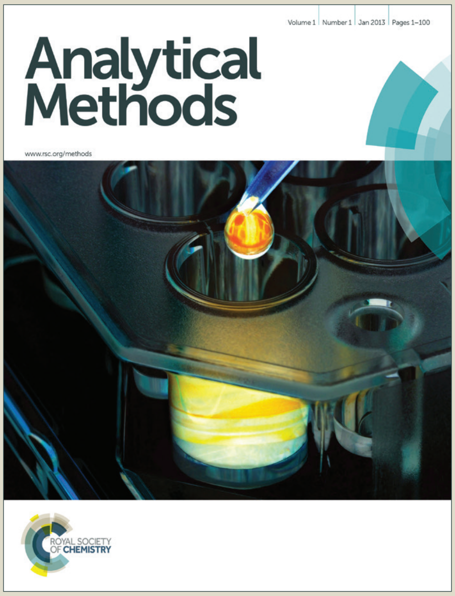

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ARTICLE TYPE

Preconcentration of ultra-trace Cu(II) and Cd(II) using SPE based on alizarin complexone modified silica gel with dectection using FAAS and dectermination of ultra-trace Cu(II) by naked eye

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Abstract

The new modified silica gel with alizarin complexone has been prepared and promised adsorbent. Ultra trace Cu(II) and Cd(II) can be selectively enriched and separated from rice and water samples by solid phase extraction and be detected by FAAS. What's more, 0.003 mol·L^{-1} and 0.25 mol·L^{-1} HNO_3 can be used as eluent for the gradient elution of Cd(II) and Cu(II), respectively. Cu(II) could be completely separated from Cd(II) and be monitored with the naked eye using color agent 5-Br-PADAP. The selectivity of adsorbent, effects of solution pH, type and concentration of eluent, foreign ions have been investigated and optimized. Under the optimized conditions, the adsorption capacity for Cu (II) and Cd (II) was 0.511 and 0.157 mmol·g^{-1}, respectively. Determination of Cu(II) and Cd(II) by FAAS was linearly in the range of 1.0-200ug·L^{-1} and 2.5–100ug·L^{-1} with a detection limit of 0.21 ug·L^{-1} and 0.46 ug·L^{-1}, respectively. Compared the determination results for Cu(II) and Cd(II) in water and rice using the new method with those detected by ICP-MS, a considerable difference wasn't observed between the two methods. And the method was validated with certified reference material GBW08511 rice. Moreover, the determination of Cu(II) in the range of 20–120 ug·L^{-1} is sensitive with the naked eye and the determination results are good in agreement with those of detected by UV-Visible spectrometry method. The proposed method was capable of determining Cu(II) and Cd(II) in real samples simply and accurately.

Introduction

Heavy metal ions, including copper and cadmium, do harm to environment and human health even at relatively low concentrations due to the fact that they can be persistent in the human vital organs and transferred into organisms by the food chain [1, 2]. Therefore, it is necessary to detect them rapidly and accurately. Flame atomic absorption spectrometry (FAAS) is largely used for the determination of metal ions [3, 4], showing good selectivity but high limit of detection. Numerous extraction and preconcentration procedures have been developed for trace and ultra trace metal ions determination in various matrices by FAAS, Such as chemical precipitation[5], liquid–liquid extraction[6], ion-exchange[7], adsorption[8], reverse osmosis[9], and membrane process[10]. By contrast, the adsorption methods have been widely used due to high efficiency especially at low concentrations, easy handling and cost effectiveness [11-13]. Among them, solid phase extraction (SPE) approach has obtained rapid acceptance owing to several major advantages in application, such as high enrichment factor, rapid phase separation, good recovery, and low consumption of reagent [14-15]. In the case of solid phase, silica gel has attracted great attention for its high mechanical and thermal stability and less susceptibility to swelling, shrinking and microbial and radiation decay [16]. In addition, the chemical modification of silica surface is possible to graft organosilyl functions to give an organic character by the silanol groups. Silica gel immobilized with various organic compounds such as thioacetamide[17], alizarin violet[18], diaminobenzidine[19], gallic acid[20] for metal ions' removal, extraction, separation and preconcentration from different matrices, have been reported. The alizarin complexone (AC) molecule provides a four coordinate chelation environment with two acetic acid groups and two vicinal hydroxyl groups [21], and has been used to chelate many metal ions for chemical analysis [22].

The contents of Cd in rice and drinking water are restricted to below 0.2mg kg^{-1} and 5ug·L^{-1}, respectively[23-24]. It is impossible to determine such low concentration Cd by FAAS without preconcentration. In this paper, the alizarin complexone modified silica gel (AC-SG) is prepared **(Fig. 1)** and promised adsorbent. The research results showed it exhibits a quick and highly efficient adsorption behavior towards Cu(II) and Cd(II). Well-known, colorimetric method has a number of advantages, such as simplicity, convenience and low cost. However, coexisting ions make the detection of Cu(II) with widely used chromogenic agent, for example 5-Br-PADAP, an impossible mission unless adding to a lot of masking reagents[25-26]. It deserves mentioning that combining the separation and enrichment capability of AC-SG, not only ultra trace Cu(II) and Cd(II) can be detected by FAAS but also ultra trace Cu(II) can be estimated using colorimetric method or naked eye which is easier, simpler and cheaper. To the best of our knowledge, using AC-SG**,** this is the first example for preconcentration of ultertrace Cu(II) and Cd(II) and monitor Cu(II) with the naked eye in real complex samples. The results of determination of Cu(II) and Cd(II) in water and rice using this proposed method are satisfactory.

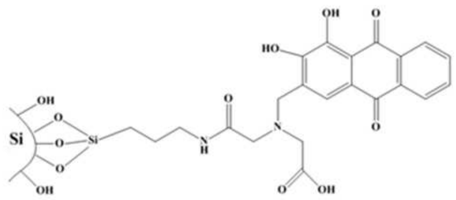

Fig.1 Chemical structure of alizarin complexone modified silica gel (**AC-SG)**

2. Experimental

2.1 Apparatus

An A1700 atomic absorption spectrophotometer equipped with various metals hollow-cathode lamps (Zhejiang Fuli Analysis Instrumentals Co., China) was used. The operating parameters of copper and cadmium for FAAS were adjusted to obtain the maximum absorbance signal. pH measurements of buffer solutions were performed using a precision acidity meter 1600 (PHS-3C, Dapu Instrumentals Co., Shanghai). A MDS-10(SINEO microwave chemistry technology Co., Ltd, China) was used for microwave-assisted digestion to decompose the samples; FTIR spectra analysis of AC-SG was recorded on a Jasco FTIR 4100 spectrophotometer. A UV-Visible spectrophotometer (GBC Scientific Equipment Pty Ltd. Cintra-2020v) was used to record absorbance. Thermogravimetric (TG) analysis was performed with a simultaneous thermal analyzer (Beijing Precision High-tech Instrument Co., LTD.ZCT-A). ICP-MS (Thermo X II) was used to analyse metal contents.

2.2 Reagents and materials

Stock standard solutions of Cd, Mg, Cr, Mn, Zn, Pb, Fe, Ni, Co, Cu at concentrations of 1000mg·L^{-1} and certified reference material (GBW08511) of rice were bought from National Standard Material Center of China. The polypropylene column tube and 20 μm PTFE sieve plates used for SPE were bought from DIKMA (Beijing, China). Working standard solutions were prepared by stepwise dilution of the stock solutions just before used. Alizarin complexone (Shanghai Aladdin reagent co., Ltd., China), γ-aminopropyltriethoxysilan (KH-550) (Lancs Research Chemicals, Ltd., America) and silica gel (20-40μm) were applied to synthesis the alizarin complexone modified silica gel. Ethanol solution of 5-Br-PADAP (2.0mmol·L^{-1}) was used as colour-developing agent. Buffer solutions of pH 1–3 or 4–6 or 7–9 was prepared by mixing appropriate ratios of 0.1M HCl and KCl, or 0.5M acetic acid and sodium acetate or 0.5M ammonia and NH_4Cl solutions. Tap water samples were collected from our laboratory after flowing for 10 min. Rice samples N-R, H-R and S-R were bought from supermarket from Zhengzhou, China. Other water samples S-N(1), S-N(2) and M-C are collected from source of south-to-north water. Doubly deionized water was used throughout the entire experiment. The pipettes and vessels used were kept in 10% (v/v) nitric acid for at least 24 h and subsequently washed four times with doubly deionized water before used. All other reagents were of analytical grade or better.

2.3 Synthesis of alizarin complexant modified silica gel (AC-SG)

10g silica gel with an excess amount of 50% (v/v) hydrochloric acid was refluxed for 6 h. It was filtered off and washed with a sufficient amount of deionised water to pH 7.0.The product was dried at 110^{o}C for 8 h. Then, 6g above pre-treated silica was taken into 100 mL toluene (which has been removed the moisture using calcium hydroxide). The addition of 6ml γ-aminopropyltriethoxysilan and 0.6mL pyridine were followed by. The mixture was refluxed for 14 h under the protection of nitrogen. The final suspension SiO_2-NH_2 was filtered off and washed with an excess amount of toluene, ethanol and acetone and dried at 80^{o}C for 12h under vacuum. For the preparation of AC-SG, 6g SiO_2-NH_2, 85mL DMF,1mL pyridine as deacid reagent, 1g EDCI superabsorbent were magnetically stirred for 1h, then 0.5g AC and 1g 1-Hydroxybenzotrizole(HOBT) as dehydrant were added and kept 2.5h in the ice water. Remove out the ice water and react for 24 hours at room temperature. The product was filtered off and washed with an excess amount of toluene, ethanol, acetone and dried at 80^{o}Cfor 12h under vacuum.

2.4 Batch method

A total of 30mg of AC-SG sorbent was added to solution with metal ions and the mixture was magnetic stirred at room temperature for 35 min to facilitate adsorption of the metal ions onto the AC-SG. The quantity of adsorbed metal on the adsorbent was calculated from the difference between the metal ion concentrations in the solution before and after sorption.

2.5 Column method

The column method was used to investigate an optimum condition for the sorption and desorption of the metal ions. The effect of solution flow rate, eluent and interfering ions were evaluated in triplicate. 50mg of functionalized silica gel adsorbent was packed in a column plugged. Before used, the column was treated by 0.5mol·L^{-1} HCl and washed with double distilled water until free from acid. Solution was adjusted to a suitable pH and percolated at a flow rate of 2.0mL·min^{-1}. Finally, the minicolumn was washed with little amount of water to remove unbounded metal ions. The adsorbed metal ions were stepwise eluted and the recovered amounts of the metal ions in eluates were determined in triplicate by FAAS or colorimetric determination.

2.6 Sample preparation

Rice samples were prepared by milling a quantity of polished to white rice flour in a food processor. White rice powder was weighed precisely and then transferred to a PFA vessel, to which 2mL of HNO_3 (65-68%) and 1mL of H_2O_2 (30%) were added and digested by microwave system. The resulting liquid was heated almost to dryness to expel the remaining HNO_3. Meanwhile blank tests for the procedure were also performed. Water samples were collected in plastic bucket containers and filtered using a 0.45 mm pore size membrane filter to remove suspended particulate matter and acidified to pH 2 by nitric acid. Then, it was stored in refrigerator at 4^oC.

2.7 Preconcentration and detemination procedure

Sample solutions were adjusted to pH 7.0 by adding $1mol\cdot L^{-1}$ NaOH and ammonia buffer and then flowed through a SPE column with $2.0mL\cdot min^{-1}$. The enriched Cu(II) and Cd(II) were eluted with 2mL 0.25 $mol\cdot L^{-1}$ HNO_3 and measured in triplicate by FAAS and ICP-MS. Moreover, the determination of Cu(II) could be done with the naked eye. Specific operations as follows: the interference of coexistence metal ions were removed in advance by sufficient $0.003mol\cdot L^{-1}$ HNO_3, then 2mL $0.25mol\cdot L^{-1}$ HNO_3 is used to elute Cu(II). The eluant was adjusted to pH 9.00 and then 0.02 mL 5-Br-PADAP was added to. Finally the solution was diluted with water to 5mL and compared with the standard color series with naked eye and UV-Visible spectrophotometer in 556nm.

3. Results and discussion

3.1 Characterization of AC-SG

To investigate the structure of the AC-SG, FTIR spectra of blank silicone and the AC-SG were measured (ESI, Fig.1-2). The broad low-frequency band centered at about 3439 cm^{-1}, followed by a weak band at 1625 cm^{-1} was attributed to O–H bond stretching vibration of Si–OH group and the adsorbed water. The intense band related to Si–O–Si stretching vibration was at 1111 cm^{-1}, and the peaks around 798 cm^{-1} and 473 cm^{-1} were due to Si–O–Si symmetric stretching and Si–O–Si bending vibrations, respectively[27]. By contrast, FT–IR spectrum of AC-SG nanoparticles displayed the new peaks at $1442cm^{-1}$ and 1362 cm^{-1} (bending vibrations of –C–N–H–)[28], 1701 cm^{-1} (stretching vibration of –C=O–) and 1635.75 cm^{-1} (stretching vibration of–N–C=O–)[29] which indicated AC were grafted onto SiO_2 nanoparticles. Moreover, Thermogravimetric (TG) analysis (ESI, Fig.3-5) showed the thermal decomposition rate of AC-SG was higher than that of blank silica gel and lower than that of AC. It indicated that AC-SG is different from AC and blank silica gel.

3.2 Selectivity of AC-SG

Selectivity is a very important parameter to evaluate the performance of AC-SG sorbent. Eleven kinds of metal ions(Cd^{2+},Cu^{2+},Cr^{3+},Ni^{+},Zn^{2+},Mg^{2+},Pb^{2+},Fe^{3+},Mn^{2+},Co^{2+},Ca^{2+}) with the same concentration ($1mg\cdot L^{-1}$) were investigated at optimal experimental conditions for their adsorption behavior on the prepared AC-SG and bare silica. The results are showed in **Fig. 2**.

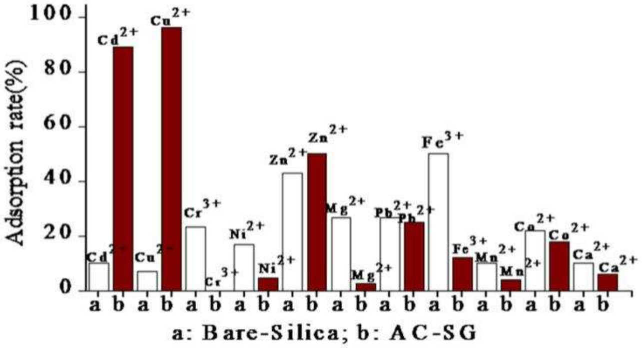

Fig.2 The adsorption behavior of different kinds of metal ions on the prepared AC-SG and bare silica: adsorbent 30mg; pH 7.00; mixing time 35min; each metal ion 30ug

It can be seen that the adsorption rate of the AC-SG for Cu(II) and Cd(II) increased by more than 90-fold compared with bare silica. In comparison, the adsorption rate for all the rest metal ions changed little. This result hint that sorption of AC-SG for Cu(II) and Cd(II) depend on coordination reaction to form Cu(II)-AC-SG or Cd(II)-AC-SG complex instead of physical absorption. So it is possible to completely separate of Cu(II) and Cd(II) from other metal ions. In this work, the research was focused on the adsorption and determination of Cu(II) and Cd(II).

3.3 Effect of pH

The major factors that influence the adsorption of Cu(II) and Cd(II) are the chelation reactions between the adsorbent and metal ions. So the number of available binding sites of AC-SG for metal ions and dissociative form of metal ions are important. These factors are very much dependent on the pH value. The effect of pH on the adsorption of Cu(II) and Cd(II) was studied. 15mL of solution($1mg\cdot L^{-1}$) with different pH value containing Cu(II) or Cd(II) was individually prepared and enriched. The results of adsorption are showed in **Fig.3**. It is obvious that adsorption of each metal ion on the modified silica increased by increasing the pH value and formed a plateau approximately in the pH range of 6.8–8.5 with adsorption rate above 90%. In theory, at a low pH value, the carboxyl groups and hydroxyl groups of AC-SG adsorbent are protonated to various degrees, decreasing the number of available binding sites for metal ions. At a high pH value, the metal ions are easy to form precipitation of hydroxide, decreasing dissociative state of metal ions. Overall consideration, for the Cu(II) and Cd(II) sorption, the medium was maintained at pH 7.0.

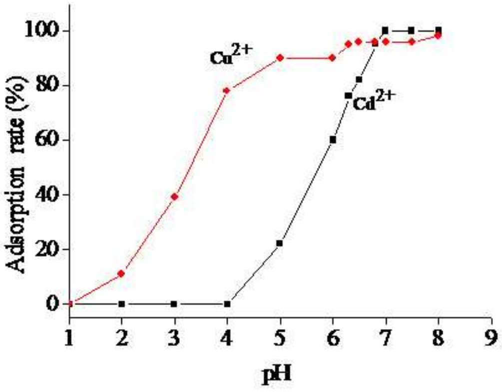

Fig.3 Effect of solution pH on the recovery of Cu(II) and Cd(II): AC-SG 30mg; mixing time 35min; Cu(II) or Cd(II)1mg·L^{-1}; solution volume 15mL.

3.4 Adsorption isotherm

Profiles of the adsorption isotherms were determined using the adsorption data through batch experiment. 30mg of AC-SG was added to 30mL of Cd(II) and Cu(II) solutions of varying concentration (10–70mg·L^{-1}), respectively. Solutions of metal ions were maintained at pH 7.0 and shaken for 35min. The initial and final metal ions in the supernatant were determined by FAAS. According to **Fig.4** and **Fig.5**, the values of the adsorption capacity (N_f) of AC-SG were 0.511mmol·g^{-1} for Cu (II) and 0.157 mmol· g^{-1} for Cd (II). When adsorption remains constant, a monolayer should be formed[30]. According to the modified Langmuir equation, the metal maximum adsorption capacity can be estimated by equation[31]:

$$C_s/N_f = C_s/N_s + 1/(N_s b) \qquad (2)$$

where C_s is the concentration of the solution in equilibrium(mmol·L^{-1}), N_f is the concentration (mmol·L^{-1}) of metal ions adsorbed on the AC-SG surface, and N_s represents the maximum amount of metal ions adsorbed per gram of material(mmol·g^{-1}). The adsorption studies were based on the linearized form of the adsorption isotherms illustrated. N_s was obtained from the angular coefficient and b from the linear coefficient of the straight lines of **Fig.6**. The values of N_s are 0.562 mmol· g^{-1} and 0.162 mmol· g^{-1} for Cu(II) and Cd(II). The similarity between the N_s and N_f values suggests that the adsorption almost reached the saturation point of the adsorption available sites.

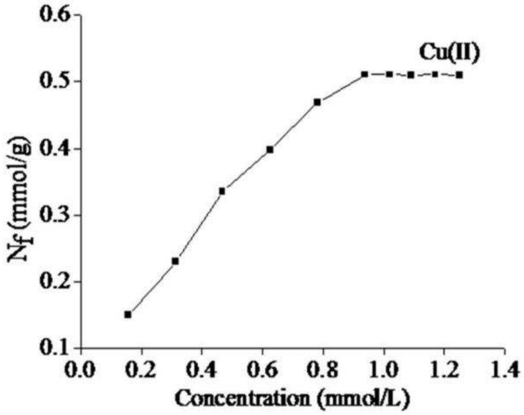

Fig.4 Isotherms of adsorption of Cu(II) onto AC-SG: AC-SG 30mg; pH7.00; mixing time 35min; solution volume 30mL

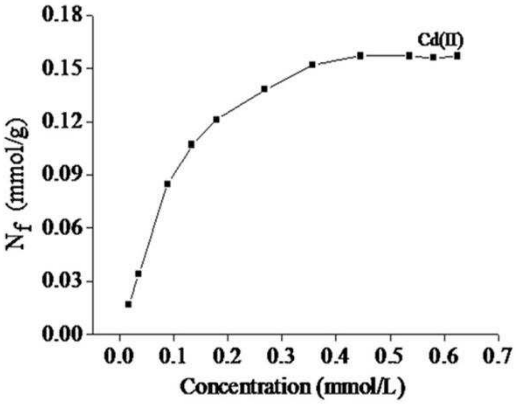

Fig.5 Isotherms of adsorption of Cd(II) onto AC-SG: AC-SG 30mg; pH7.00; mixing time 35min; solution volume 30mL.

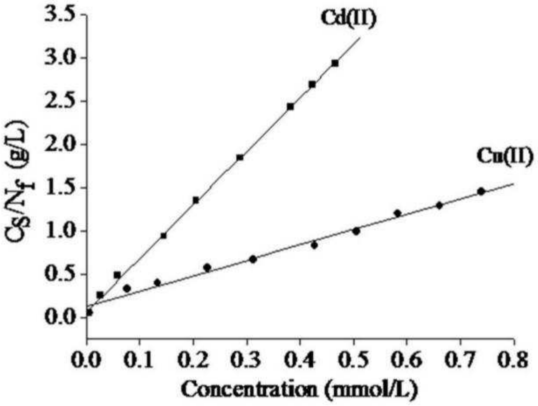

Fig.6 Linearization of adsorption isotherms of Cu(II) and Cd(II)

3.5 Effect of of eluent

The effects of HNO_3, HCl and H_3PO_4 as eluents on desorption of metal ions were studied, respectively. Aliquots of 10mL of 100 ug·L^{-1} metal ion solution were passed through the AC-SG minicolumn at flow rate 2mL·min^{-1}. As compared to the eluent types at equal concentration, the elution with HNO_3 seemed to be more effective and favorable for the quantitative recovery of Cu(II) and Cd(II) desorption. To optimize eluent concentration,

concentration of HNO_3 was varied from $0.001 mol·L^{-1}$ to $0.3 mol·L^{-1}$ to desorb Cu(II) and Cd(II). Results indicate that the recovery of Cd(II) is more than 90% with 2mL of $0.003 mol·L^{-1}$ HNO_3 as eluent. By contrast, there was no detectable copper. As can be seen in **Table 1**, for Cu(II), by increasing the concentration of the acid up to $0.2\sim0.3 mol·L^{-1}$, recoveries stayed approximately constant. Accordingly, a concentration of $0.25 mol·L^{-1}$ HNO_3 was selected as the optimum for the subsequent work. It is worth noting that enough $0.003 mol·L^{-1}$ HNO_3 is capable to elute all interfering metal ions from sorbent-packing SPE column except Cu. This is extremely valuable for the further colorimetric determination.

Tab. 1. Effect of eluent concentration on the desorption of metal ions

$C_{(HNO3)}$ $(mol·L^{-1})$	0.001	0.002	0.003	0.005	0.01	0.1	0.2	0.3
Rec.(%) of Cd	50	87	92	93	93	93	96	96
Rec.(%) of Cu	-	-	-	15	60	78	93	93

"-" means not detected.

3.6 Effect of coexisting ions

The effect of foreign ions coexisting with Cd(II) and Cu(II) on AC-SG adsorption was shown in **Table 2**. 10mL of the test solution containing $100 ug·L^{-1}$ of the studied heavy metal ions and other ions at various concentrations was passed through the column under optimum conditions. The amount of target heavy metal ions extracted was determined by FAAS after elution. The tolerance limit was taken as the maximum concentration of the foreign substances which caused an approximately ±10% relative error in the determination. At the maximum tolerance concentration, $0.003 mol·L^{-1}$ HNO_3 can desorb more than 99% Pb, Zn, Fe and more than 97% Ni, Co. The results showed that a lot of coexisting ions don't influence the preconcentration and determination of Cu(II) and Cd(II).

Tab. 2. Effect of foreign ions on Cu(II) and Cd(II)

Coexisting ions	$[M]/[Cd^{2+}]$	Recovery of Cd (%)	$[M]/[Cu^{2+}]$	Recovery of Cu (%)
Na^+	10000	98.6	10000	100.0
Ca^{2+}	1000	100.5	1000	102.0
Mg^{2+}	800	109.0	800	107.8
Zn^{2+}	75	105.6	75	104.6
K^+	10000	103.7	10000	98.6
Ba^{2+}	100	98.6	100	101.1
Fe^{2+}	50	105.0	50	95.3
Fe^{3+}	100	100.0	100	100.0
Ni^{2+}	100	100.1	100	100.0
Pb^{2+}	50	109.8	50	109.6
Co^{2+}	45	101.2	45	110.0
Cl^-	10000	103.7	10000	98.6
NO_3^-	10000	109.8	10000	105.6
SO_4^{2-}	800	97.8	800	95.7
NH_4^+	10000	96.3	10000	98.4
$H_2PO_4^-$	10000	98.3	10000	96.0

3.7 Reusability of the AC-SG

To investigate the reusability of the AC-SG, preconcentration efficiencies of Cd(II) and Cu(II) using regenerative AC-SG as sorbent were determined by FAAS. After dozens of times regeneration of AC-SG, the recovery efficiencies of Cd(II) and Cu(II) still maintain above 90%, which indicate that the adsorbent has excellent stability and reusability.

3.8 Characteristic of method

Preconcentrate of ultra trace Cu(II) and Cd(II) in large volume solution is entirely feasible by the column equipped with the AC-SG, but it need more time. When the volume is 30mL, the linear range obtained were 1.0-200 $ug·L^{-1}$ and 2.5-100 $ug·L^{-1}$ with a correlation coefficient of 0.995 and 0.999 for Cu(II) and Cd(II), respectively. The relative standard deviation (n=9) for $50 \mu g·L^{-1}$ of Cu(II) and Cd(II) were 2.8% and 3.4%, respectively. When the volume of loading sample is 100mL, the detection limits (LOD) of Cu(II) and Cd(II) calculated as three times the standard deviation of the blank signals (n=9) were $0.21 ug·L^{-1}$ and $0.46 ug·L^{-1}$, respectively.

3.9 Application to real samples

(1) Detection of Cu(II) and Cd(II) by FAAS

In order to validate the proposed method, a certified reference material (GBW08511) of rice with certified value of Cd(II) $0.504\pm0.018 mg·kg^{-1}$ was analyzed. The value determined by the proposed method of Cd(II) and Cu(II) was $0.500 mg·kg^{-1}$ and $1.86 mg·kg^{-1}$, respectively. The R.S.D. of three replicates was 3.8% for Cd(II), and for Cu(II) was 2.6 %.The proposed method was applied to the determination of Cd(II) and Cu(II) in real water and rice samples. 100 mL of each water sample and 0.25g of each rice sample were pre-treatment as described in 2.6 and 2.7 and detected by the new method and ICP-MS method. The analysis results are shown in **Table 3** and **Table 4**. Some of the analytes were spiked with Cu(II) and Cd(II) standards to assess matrix effects. The recoveries of Cu(II) and Cd(II) spiked in samples were between 90% and 110%. The relative standard deviations are not more than 5%. When the confidence level is 95%, the number of measurement is three, critical values(t_{crt}) of t-test about table 3 and table 4 were 2.92 and 4.30, respectively. Compared the determination results for Cu(II) and Cd(II) in water and rice samples using the proposed method with those detected by ICP-MS by t-test. The calculated t values are in the range of 1.10~2.86 about table 3 and 0.62~3.98 about table 4 which are lower than the critical t_{crt}. It shows that there is not significant difference between the two methods.

Tab.3.Determination results of Cu(II) and Cd(II)in water(n=3)

Analyte	Samples	Spiked $(ug·L^{-1})$	Result $(ug·L^{-1})$	Rec. (%)	RSD (%)	ICP-MS $(ug·L^{-1})$	RSD (%)
Cd	S-N(1)	0.0	0.60		4.0	0.56	1.2
		2.0	2.43	91.5	3.6		
	S-N(2)	0.0	<0.46		4.1	0.12	2.1
		2.0	1.92	96.0	4.0		
	M-C	0.0	<0.46		4.2	0.20	2.0
		2.0	1.84	92.0	3.3		
Cu	S-N (1)	0.0	2.50		3.0	2.46	1.2
		5.0	7.26	95.2	2.6		
	S-N(2)	0.0	2.80		3.8	2.69	1.5
		5.0	8.10	106.0	2.9		
	M-C	0.0	5.20		3.6	5.08	1.3
		5.0	9.98	95.6	3.0		

Tab.4.Determination results of Cu(II) and Cd(II)in rice(n=3)

Analyte	Samples	Spiked ($mg\cdot kg^{-1}$)	Result ($mg\cdot kg^{-1}$)	Rec. (%)	RSD (%)	ICP-MS ($mg\cdot kg^{-1}$)	RSD (%)
Cd	N-R	0.0	<0.004		4.2	0.004	2.8
		0.4	0.39	97.5	4.2		
	H-R	0.0	<0.004		4.7	0.002	2.5
		0.4	0.37	92.5	3.9		
	S-R	0.0	0.08		4.2	0.072	1.9
		0.4	0.51	107.0	2.1		
Cu	N-R	0.0	2.48		3.6	2.37	1.3
		3.0	5.68	106.7	2.6		
	H-R	0.0	2.99		4.0	2.86	2.0
		3.0	5.73	91.3	3.2		
	S-R	0.0	3.69		3.0	3.73	1.8
		3.0	6.56	95.6	1.5		

(2) Rapid colorimetric detection of Cu(II) by naked eye

The concentration of Cu(II) in samples can be determined by colorimetric method with the naked eye because the interfering metal ions in samples, including Cd(II), can be removed by 0.003mol·L^{-1} HNO_3 in advance and in the 0.25 mol·L^{-1} HNO_3 eluent, could not be detected by FAAS except Cu(II). With the increasing in Cu(II) concentrations in solution, obvious color changes from yellow to red can be observed. To validate the practical application of Cu(II) detection system, the concentration of Cu(II) in real water(25mL) and rice(0.08g) samples was measured by naked eye and UV-Visible method. Meanwhile, 4.5 mL of untreated tap water was tested and the result is higher than real value due to the effect of coexisting ions. When the tap water and rice were treated by the proposed method, the results are similar to those by UV-Visible spectrophotometer. When the water of 25mL was enriched and test in 5mL, the detection limits (LOD) of Cu(II) by UV-Visible spectrophotometer calculated as three times the standard deviation of the blank signals (n=9) were 0.036ug·L^{-1}. The limit of quantification by naked eye is 1.6ug·L^{-1}. The proposed method was used to determine Cu(II) in water and rice samples(**Table 5**)

Tab. 5. Determination results of Cu(II)

Samples	Results (naked eye)	Results (UV-Vis.)	RSD (%)
Tap water	5.00-6.00 (ug·L^{-1})	5.60(ug·L^{-1})	2.2
M-C water	4.00-5.00 (ug·L^{-1})	4.80(ug·L^{-1})	2.7
H-R rice	2.81-3.13 (mg·kg^{-1})	2.81(mg·kg^{-1})	4.6

Tab. 6. Comparison table of proposed method with published articles by SPE

Complexing agent	Tested elements	LOD for Cu (ug·L^{-1})	LOD for Cd (ug·L^{-1})	Literature	Preconcentration factor
bis(3-aminopropyl)amine	Cu	0.12	-	[32]	150, -
thiourea	Cu, Cd	0.38	0.81	[33]	-, -
ionic liquid-modified composite	Cu, Cd	0.3	0.1	[34]	-, -
1-(2-thiazolylazo)-2-naphthol	Cu, Cd	0.77	0.57	[35]	200, 100
ETPD	Cu	0.25	-	[36]	400, -
Polyethyleneimine	Cu	0.15	-	[37]	100, -
1,10-phenanthroline	Cu, Cd	0.04	0.14	[38]	-, -
alizarin complexone	Cu, Cd	0.21	0.46	[this paper]	50, 50

"-"means there was no this data in article

4. Conclusions

In this study, an SPE-based procedure for the pre-concentration of ultra trace and trace of Cu(II) and Cd(II) was developed. When combined with FAAS, the LOD of Cu(II) and Cd(II) are 0.21 ug·L^{-1} and 0.46 ug·L^{-1}, respectively. The proposed method there is a compared detection limit for Cu with many methods previously published by SPE(**Table 6**). More importantly, Cu(II) can be determined by 5-Br-PADAP with naked eye and this colorimetric method could provide a promising reliable assay in real environmental samples. Predictably, the developed method is also applicable in monitoring Cu(II) and Cd(II) in other food or environmental samples owing to its facile and accurate features.

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Notes and references

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† Electronic Supplementary Information (ESI) available for FTIR Fig. 1-2

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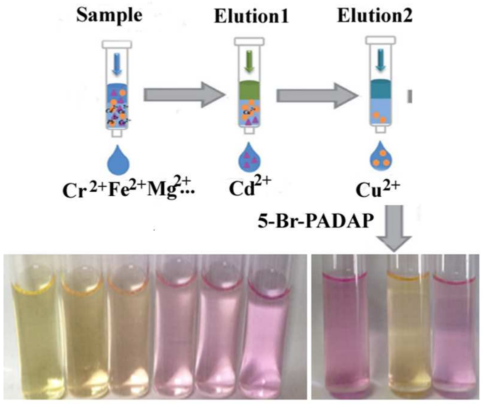
Graphical Abstract:



By the gradient elution of Cu(II) and Cd(II), enriched Cu(II) could be completely separated from Cd(II) and be monitored with the naked eye using color agent 5-Br-PADAP.

Captions

Figure 1: Chemical structure of alizarin complexant modified silica gel (**AC-SG)**

Figure 2: The adsorption behavior of different kinds of metal ions on the prepared AC-SG and bare silica: adsorbent 30mg; pH=7.00; mixing time 35min; each metal ion 30ug.

Figure 3: Effect of solution pH on the recovery of Cu(II) and Cd(II): AC-SG 30mg; time 35min; Cu(II) or Cd(II)1mg·L^{-1}; solution volume 15mL.

Figure 4: Isotherms of adsorption of Cu(II) onto AC-SG: AC-SG 30mg; pH=7.00; mixing time 35min; solution volume 30mL.

Figure 5: Isotherms of adsorption of Cd(II) onto AC-SG: AC-SG 30mg; pH=7.00; mixing time 35min; solution volume 30mL.

Figure 6: Linearization of adsorption isotherms of Cu(II) and Cd(II)

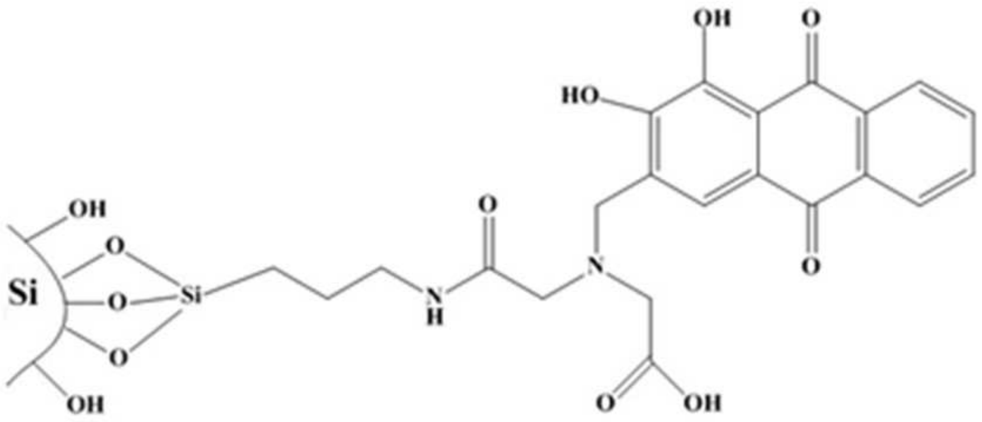


Figure 1

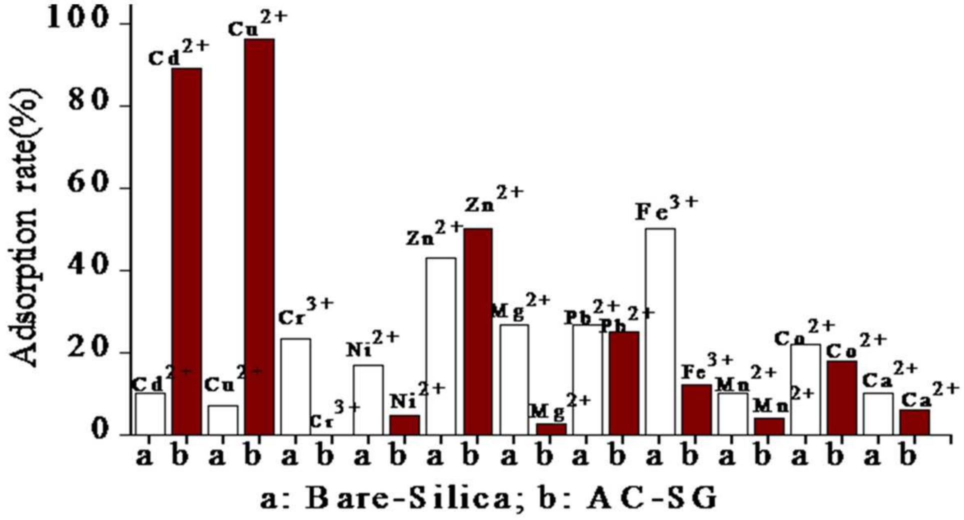


Figure 2

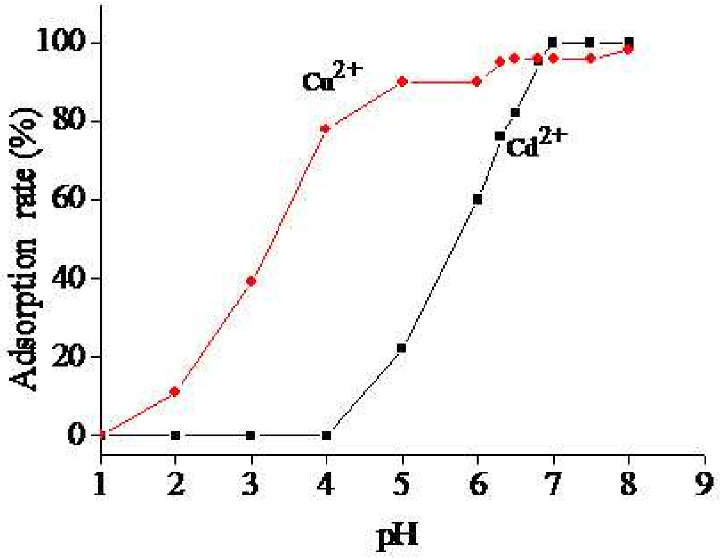


Figure 3

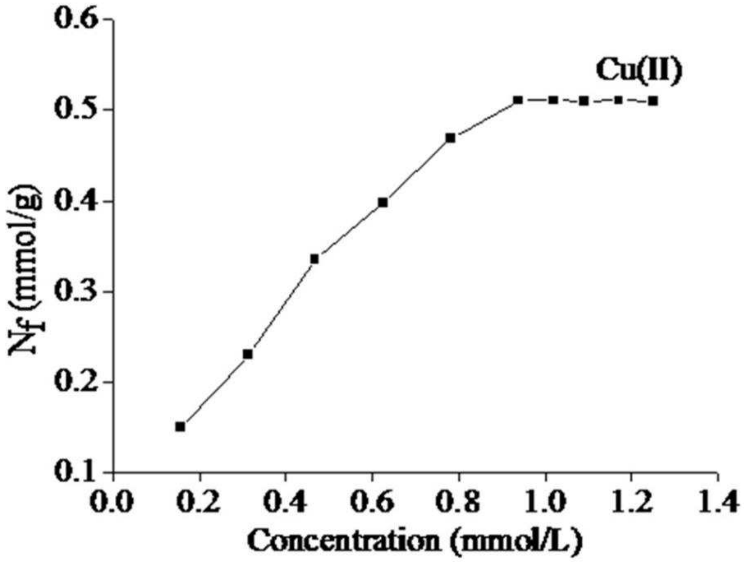


Figure 4

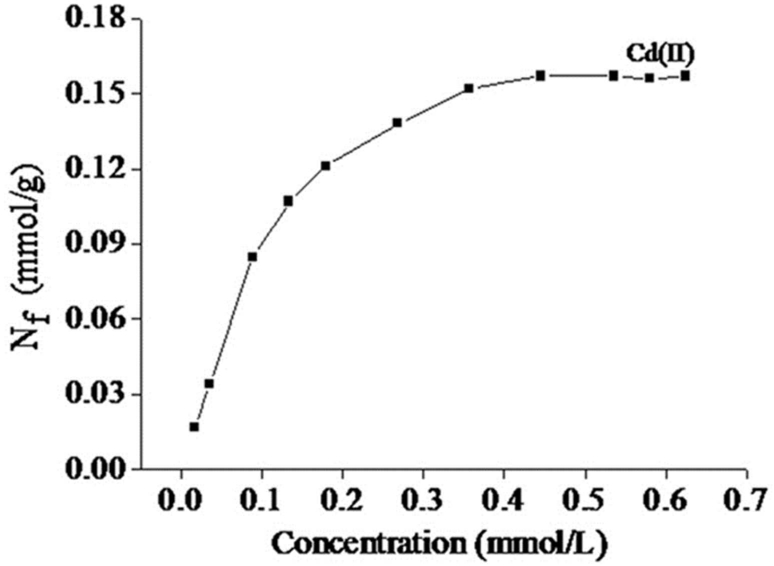


Figure 5

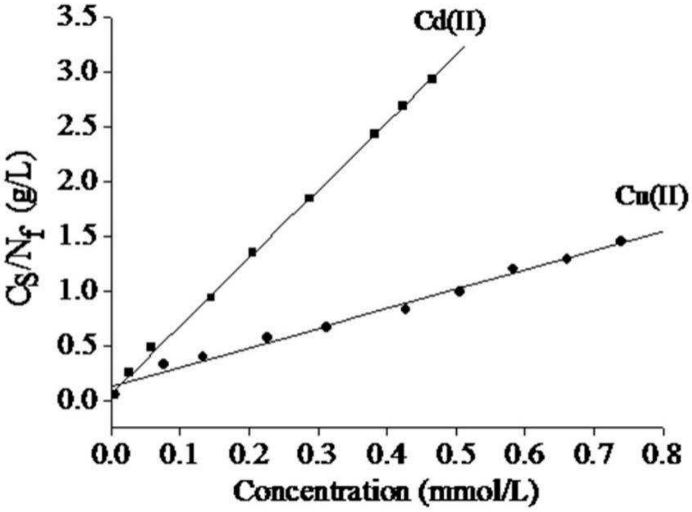


Figure 6