

Solid Phase Extraction and Flame Atomic Absorption Spectrometry for the Determination of Trace Cadmium

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A method was developed for the separation and preconcentration of Cd(II) ions based on its complex formation with 2-(2-quinolinylazo)-4-methyl-1,3-dihydroxydibenzene (QAMDHB) loaded on graphitized carbon black as sorbent in a cartridge. The preconcentrated ions were eluted from the cartridge using 2.0 mL of 0.5 mol L⁻¹ HNO₃ solution as eluant and then the Cd(II) contents was measured by flame atomic absorption spectrometry. The conditions for preparation of the graphitized carbon black loaded with QAMDHB, pH of sample solution, sample volume, the concentration of washing solution, sample flow-rate through the cartridge, capacity of the modified graphitized carbon black and the effect of matrix on the preconcentration were carefully studied. A preconcentration factor of 500 was achieved under the optimum conditions and the detection limit of the method reached 0.05 µg L⁻¹ for Cd(II). The method was successfully applied to the determination of cadmium(II) in tobacco, soil and water samples. The relative standard deviations were below 3.2 % with recoveries of 91-98 %. The determination results were agreed with that of reference method (ICP-MS method).

Key Words: Cadmium, Graphitized carbon black, Solid phase extraction, 2-(2-quinolinylazo)-4-methyl-1,3-dihydroxydibenzene, FAAS.

INTRODUCTION

Cadmium is a highly toxic element which has been described as one of the most dangerous elements in the biological system and environment^{1,2}. The Chinese Standards for Environment requires that the concentration of cadmium should not be exceeded 0.01 mg L⁻¹ in water and 0.1 mg kg⁻¹ in food³. Therefore, the determination of traces cadmium in biological and environmental samples is very important. The atomic absorption (AAS) and emission spectrometry are the most widely methods used for trace cadmium determination^{4,5}. Flame atomic absorption spectrometry (FAAS) is a simple technique. However, the determination of traces cadmium by FAAS in complex matrices is difficult due to its low sensitivity and the interfering effects of matrix components⁶⁻⁸. Hence, a previous separation and preconcentration steps are frequently requires. The most widely used preconcentration methods are coprecipitation, ion exchange, solvent extraction, flotation and solid phase extraction (SPE)⁹⁻¹¹.

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Solid phase extraction (SPE) is an attractive separation-preconcentration technique for heavy metal ions with some important advantages (simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents and environment friendly). Various solid phase extraction materials have been successfully used for the preconcentration and separation of cadmium at trace levels¹²⁻¹⁴. At this point, graphitized carbon black has been proposed as a novel solid phase extraction sorbents for various inorganic and organic materials at trace levels. The graphitized carbon black possesses excellent adsorption ability because of their large specific surface area^{15,16}. However, the application of graphitized carbon black as sorbent for separation and preconcentration trace cadmium has received little attentions.

A relatively simple alternative for preparation of the solid phase is based upon the impregnation of reagents on solid supports. 2-(2-quinolinylazo)-4-methyl-1,3-dihydroxydibenzene (QAMDHB) is a spectrophotometric reagent for cadmium in our laboratory. It can react with cadmium at room temperature rapidly^{17,18}. In this work, it is noted that QAMDHB can also be adsorbed on graphitized carbon black surfaces and thus, the adsorbed QAMDHB did not wash away during the elution step. This means that the graphitized carbon black cartridge can be used several times without decreasing the enrichment factor. Based on this, a separation and preconcentration method for the determination of cadmium by FAAS using graphitized carbon black as sorbent and QAMDHB as complexing agent was developed.

EXPERIMENTAL

Carbopack™ B graphitized carbon black (60-80 mesh) was obtained from Sigma-Aldrich Corporation (USA). All solutions were prepared with double distilled water. Otherwise stated, analytical-grade acids and other chemicals were obtained from Merck (Darmstadt, Germany). QAMDHB solution, 1.0 % (m/v), was prepared by dissolving 0.1 g of the reagent in ethanol. Universal buffer (pH 3.0-11.0) was made of mixture of acetic acid, boric acid and phosphoric acid and sodium hydroxide (0.01 mol L⁻¹) in water.

The certified reference materials: Tobacco (GBW08514), human hair (GBW08126), seawater (GBW(E)080040 and soil sample (GBW(E)070042) were obtained from the Chinese Standard Center. The drinking water was collected at Kunming, P.R. China. All samples solution for analysis were filtered through a cellulose membrane of pore size < 0.45 μm.

Preparation of modified graphitized carbon black cartridge: In a 50 mL beaker, 10.0 g of graphitized carbon black was added to 10 mL of QAMDHB ethanol solution (1.0 %) and mixed well. The ethanol was evaporated and the modified graphitized carbon black was obtained. A teflon cartridge (0.8 cm length and 0.5 mm in diameter, Fig. 1.) was packed with 0.25 g of the modified graphitized carbon black.

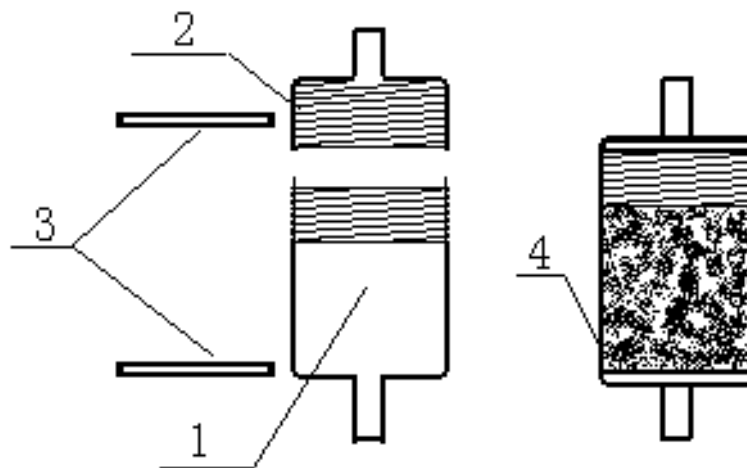


Fig. 1. Solid phase extraction cartridge (1) Tube for fill in the sorbent, (2) Screw cap for sealing the tube), (3) Sieve plate, (4) modified graphitized carbon black

A Perkin-Elmer Model A Analyst 600 atomic absorption spectrometer equipped with a Model AS-800 autosampler (Norwalk, CT) and furnished with a cadmium hollow-cathode lamp was used. The instrument was adjusted according to the standard conditions: Lamp current 8 mA, wavelength 228.8 nm, air-acetylene flame (air flow rate 15 L min⁻¹, acetylene flow rate 1.8 L min⁻¹), spectral band width 0.7 nm. The pH of aqueous solutions was checked using a Beckman F-200 pH meter with a glass electrode.

Procedure: The method was tested with model solution before its application to real samples. A 50-1000 mL of Cd(II) solution, buffered at pH 6.0 (universal buffer, 0.01 mol L⁻¹), was passed through the cartridge at a flow rate of 10.0 mL min⁻¹. After finishing the sample solution, a volume of 2.0 mL of 0.5 mol L⁻¹ HNO₃ was passed through the cartridge in the reverse direction at a flow rate of 2.0 mL min⁻¹ to elute the Cd(II) ions. The per cent of cadmium ions adsorbed on the cartridge for the concentration of Cd(II) was calculated from the amount of Cd(II) ions in the starting sample and the amount of Cd(II) eluted from the cartridge.

For seawater and drinking water, the pH of the sample was adjusted to 6.0 and the solution was passed through the cartridge. Cadmium ions retained on the cartridge were eluted with 2.0 mL of 0.5 mol L⁻¹ HNO₃. The eluent was analyzed by the flame atomic absorption spectrometry.

For soil sample, 0.1 g of sample was decomposed with 6.0 mL of aqua regia and the solution was evaporated to dryness. This process was repeated twice. A volume of 10 mL of distilled water was added to the residue. The suspension was filtered through a blue band filtering paper and the insoluble residue was washed with distilled water. Afterwards, the above preconcentration procedure was applied to the final solutions and the blank solution.

For biological samples, 0.25 g of sample was weighed accurately into the 25 mL Teflon high-pressure microwave acid-digestion bomb. To which, 3.0 mL of concentrated nitric acid and 3.0 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 10 mL of 5 % HCl and the pH of the sample was adjusted to 6.0 with 5 % NaOH. Afterwards, the above preconcentration procedure was applied to the final solutions and the blank solution.

RESULTS AND DISCUSSION

Optimization of variables: First of all, to obtain the best quantitative recoveries of Cd(II) ions, many parameters such as pH of sample solution, sample volume, the concentration of washing solution, sample flow-rate through the cartridge, capacity of the modified graphitized carbon black and the effect of matrix on the preconcentration step should be studied.

In the optimization steps, 0.25 g of graphitized carbon black was used. The influence of sample solution pH on the preconcentration step of Cd(II) was studied. For this purpose, 200 mL of 0.05 mg mL^{-1} Cd(II) at different pH values (3.0-10.0) was passed through the modified solid phase. Then the Cd(II) concentration in eluent solution was checked by FAAS. The results (Fig. 2) showed that the suitable pH for adsorption of Cd(II) on the modified graphitized carbon black is around 5.5-8.0. Therefore, a buffer solution (universal, 0.01 mol L^{-1}) at pH 6.0 was used for the preconcentration step.

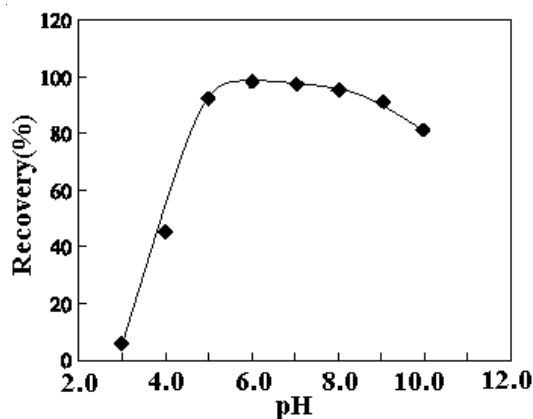


Fig. 2. Influence of pH of the sample solution on adsorption of Cd(II) on the modified graphitized carbon black. Conditions: Initial Cd(II) value, 200 mL of $0.05 \text{ } \mu\text{g mL}^{-1}$; Washing solution, 2.0 mL of $0.50 \text{ mol L}^{-1} \text{ HNO}_3$.

For desorption of Cd(II) from the solid phase, different HNO_3 concentrations (2.0 mL) in the interval range of 0.2 to 2.0 mol L^{-1} with flow rate of 2.0 mL min^{-1} were tested for the quantitative elution of the adsorbed Cd(II) ions from the cartridge.

The results (Fig. 3) showed that $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ was suitable to remove (100 ± 1.3) % of Cd(II) from the solid sorbent. In order to optimize the volume of $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ solution, 50 mL of $0.2 \text{ mg mL}^{-1} \text{ Cd(II)}$ was passed through a series of the modified graphitized carbon black under the optimum conditions. Then the solid phases were washed with different volumes of $0.50 \text{ mol L}^{-1} \text{ HNO}_3$ (1.0 -10.0 mL). The results showed that it is easier to elute the retained Cd(II) from cartridge in the reverse direction in comparison to the forward direction (Only 2.0 mL of HNO_3 solution was needed when eluted in reverse direction. However, 8 mL of HNO_3 solution was needed when eluted in forward direction). Thus, it is also recommended to invert the cartridge before elution (Fig. 4).

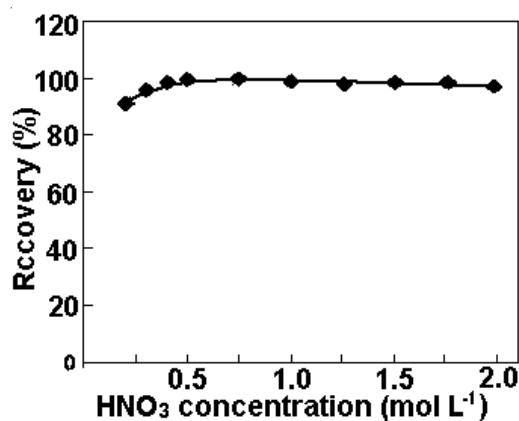


Fig. 3. Influence of HNO_3 concentration on the elution of the adsorbed Cd(II) from the cartridge. Conditions: Cd(II) adsorbed is $10 \mu\text{g}$. The flow rate of eluant is 2.0 mL min^{-1}

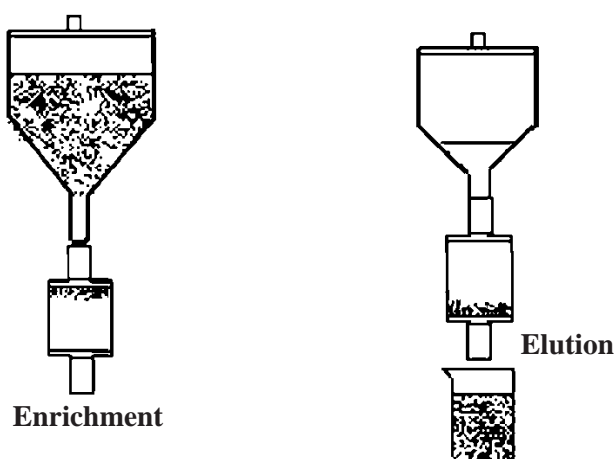


Fig. 4. Eluting the Cd(II) ions in the reverse direction

The influence of the sample flow rate on preconcentration efficiency of Cd(II) ions through the cartridge was also investigated. For this purpose, a volume of 50 mL of $0.2 \mu\text{g mL}^{-1}$ Cd(II) solution at pH 6.0 was passed through a series of cartridge at different flow rates. Then the adsorbed Cd(II) was washed with 2.0 mL of 0.5 mol L^{-1} HNO_3 solution and the Cd(II) content was measured using FAAS. The results (Fig. 5) showed that using a sample flow rate greater than 12 mL min^{-1} can caused a decrease of the Cd(II) ions recoveries. Therefore, a sample flow rate of 10.0 mL min^{-1} was used for further studies.

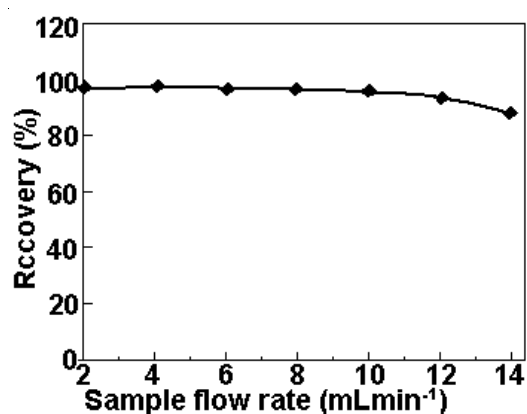


Fig. 5. Influence of sample flow rate on the preconcentration efficiency of Cd(II) ions. Conditions: Volume of sample is 50 mL and Cd(II) concentration is $0.2 \mu\text{g mL}^{-1}$

The effect of flow rate of HNO_3 solution (0.5 mol L^{-1}) on desorption efficiency of Cd(II) ions from the cartridge was also checked in the range of $1.0\text{-}5.0 \text{ mL min}^{-1}$. The results (Fig. 6) showed that the recovery of cadmium was maximized when using elution rates up to $1.0\text{-}2.5 \text{ mL min}^{-1}$. Therefore, 2.0 mL min^{-1} was selected.

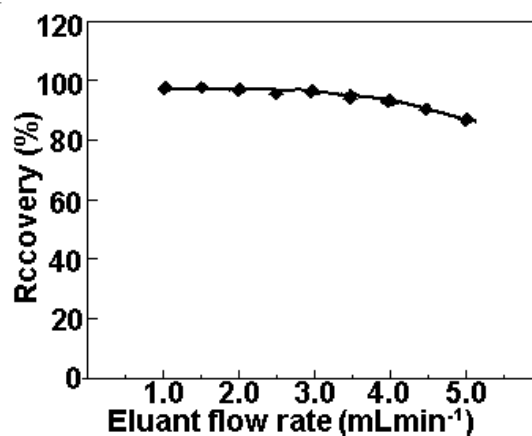


Fig. 6. Effect of eluant (0.5 mol L^{-1} HNO_3) flow rate on desorption efficiency of Cd(II). Conditions: Cd(II) adsorbed is $10 \mu\text{g}$. The volume of eluant is 2.0 mL

The capacity of the modified graphitized carbon black for adsorption of Cd(II) was checked by passing 150 mL of Cd(II) solution containing 0.05-10 $\mu\text{g mL}^{-1}$ Cd(II) through the cartridge (containing 0.25 g modified graphitized carbon black). The metal ions were stripped off the modified graphitized carbon black with 2.0 mL 0.5 mol L⁻¹ HNO₃ and measured by FAAS. The results were showed in Fig. 7. Under the condition of cadmium recovery $\geq 95\%$, the adsorption capacity was calculated to be 0.8 mg g⁻¹. The cartridge has adequate capacity to enrich the cadmium in real sample.

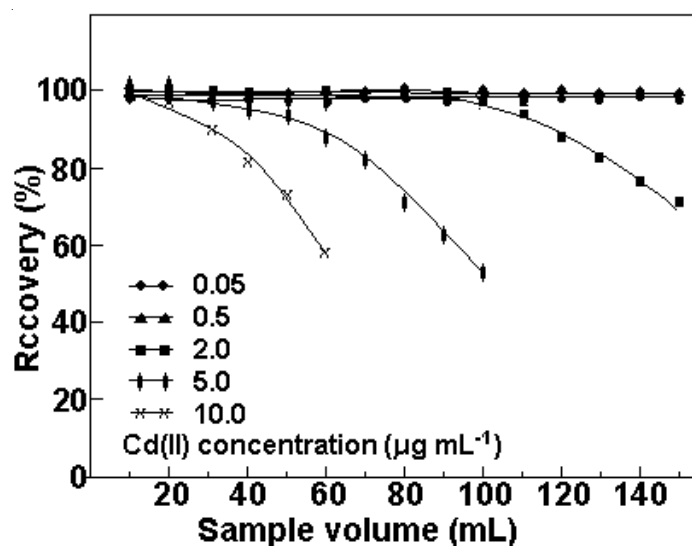


Fig. 7. Effect of sample volume on the adsorption efficiency of Cd(II). Conditions: The modified graphitized carbon black is 0.25 g, other conditions as in the preconcentration procedure

Reusability of the modified graphitized carbon black was checked using the same solid phase for sorption-desorption of Cd(II) ions for 50 times the reusability was tested. The maximum change in the performance (sorption capacity) of the solid phase after the repeated use was less than 2%, indicating that its repeated use is feasible as leaching of the dye from the graphitized carbon black matrix is insignificant. No change in the sorption capacity of the modified graphitized carbon black was noticed after storing it for 5 months.

Calibration graphs and detection limits: Under the FAAS analysis conditions, regression equations of metal ions were established based on the standard samples injected and their absorption signals. The results showed that the linearity range for cadmium was obeyed in the range of 0.01-4.0 $\mu\text{g mL}^{-1}$ and the linear regression equation obtained was: $A = 0.0272 + 0.568 C$ ($\mu\text{g mL}^{-1}$), $r = 0.9995$.

The results showed that the limit of quantitative preconcentration was $0.2 \mu\text{g L}^{-1}$ Cd(II) with a preconcentration factor of 500 (1000 mL of sample solution was passed the cartridge). Recoveries from further diluted solutions or larger sample volume were not quantitative (the recovery of cadmium $< 95\%$). The limit of detection values based on three times the standard deviations of the blank was equal to $0.05 \mu\text{g L}^{-1}$ Cd(II).

Interference study: The influence of matrix ions in samples on the separation and recovery of Cd(II) ions was also investigated by passing different amounts of potential interfering ions plus 50.0 ng mL^{-1} Cd(II). The results showed that 10000-fold of alkaline and alkaline-earth ions, chloride, nitrate, hydrogen carbonate, carbonate and sulfate, 500-fold Zn(II), Fe(II), Ni(II), Pd(II), V(III), Mn(II), Cu(II), Hg(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), Pb(II), did not interfere. The results confirm that the interference ions do not absorbed on the solid phase or the ions which absorbed on the solid phase do not reach the interference amount for AAS determination.

Application to real samples: The method was applied to the determination of cadmium in biological samples, water and soil. The results (deducted the reagents blank) were given in Table-1 for biological samples and were given in Table-2 for water and soil samples. For water and soil samples, an ICP-MS method¹⁹ had also been used as reference method and the result were also shown in Table-2.

TABLE-1
DETERMINATION RESULTS OF CERTIFIED STANDARD BIOLOGICAL SAMPLES

Samples	Standard value ($\mu\text{g g}^{-1}$)	Present method ($\mu\text{g g}^{-1}$)	RSD (%) (n = 7)	Recovery (%) (n = 5)
Tobacco (GBW08514)	Ag (0.164), As (0.292), B (68.2), Bi (0.368), Ca (2900), Cd (0.218), Ce (1.36), Co (4.71), Cr (3.47), Cu (9.82), Fe (48.6), Hg (0.067), Mg (524), Mn (19.6), Mo (0.862), Ni (3.58), Pb (0.863), V (2.78), Zn (15.8)	0.226	3.0	93-98
Human hair (GBW08126)	Ag (-), As (0.121), B (38.4), Bi (0.825), Ce (0.643), Cd (0.528), Co (6.25), Cr (0.816), Cu (11.2), Fe (123), Hg (0.142), Mg (136), Mn (68.2), Ni (5.61), Pb (1.06), Sn (1.24), Se (0.0412), V (3.86), Zn (18.7)	0.514	2.8	92-96

TABLE-2
DETERMINATION RESULTS OF THE WATER AND SOIL SAMPLES

Samples	ICP-MS method ($\mu\text{g/L}$)	Present method ($\mu\text{g/L}$)	RSD (%) (n = 7)	Recovery (%) (n = 5)
Drinking water	1.220	1.340	3.2	89-96
Seawater ^a	0.492	0.468	2.8	91-94
Soil ^b	1.180	1.220	3.0	92-97

^a Certified value: $0.47 \pm 0.03 \mu\text{g L}^{-1}$; ^b Certified value: $1.26 \pm 0.02 \mu\text{g g}^{-1}$.

Conclusion

The developed method is successfully employed for analysis of water, soil and biological samples after successful validation. The developed method has the following characters: (1) The method is economic. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of the modified graphitized carbon black was as high as greater than 50 cycles without any loss in its sorption behaviour. (2) The elution was easily performed with 0.5 mol L⁻¹ HNO₃ and the metal ions in 1000 mL solution can be concentrated to 2.0 mL, representing an enrichment factor of 500 was achieved. The analytical performance of the method is comparable with other separation-preconcentration methods. The limits of detection of analyte ions are superior to those of some preconcentration/separation techniques for analyses^{6-8,20,21}. (3) For real samples determination, the relative standard deviations were below 3.2 % and the recoveries of Cd(II) were in the range of 91-98 %. The recoveries obtained by the present solid phase are also comparable with the widely used and recently reported solid phase extraction sorbents. (4) The matrix effects with the method were reasonably tolerable. The method is also relatively rapid as compared with previously reported procedures for the enrichment of traces metal ions.

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