

On-line solid phase selective separation and preconcentration of Cd(II) by solid-phase extraction using carbon active modified with methyl thymol blue

Ali A. Ensafi*, Ali R. Ghaderi

College of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

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Abstract

An on-line flow system was used to develop a selective and efficient on-line sorbent extraction preconcentration system for cadmium. The method is based on adsorption of cadmium ions onto the activated carbon modified with methyl thymol blue. Then the adsorbed ions were washed using 0.5 M HNO₃ and the eluent was used to determine the Cd(II) ions using flame atomic absorption spectrometry. The results obtained show that the modified activated carbon has the greatest adsorption capacity of 80 μg of Cd(II) per 1.0 g of the solid phase. The optimal pH value for the quantitative preconcentration was 9.0 and full desorption is achieved by using 0.5 M HNO₃ solution. It is established that the solid phase can be used repeatedly without a considerable adsorption capacity loss. The detection limit was less than 1 ng mL⁻¹ Cd(II), with an enrichment factor of 1000. The calibration graph was linear in the range of 1–2000 ng mL⁻¹ Cd(II). The developed method has been applied to the determination of trace cadmium (II) in water samples and in the following reference materials: sewage sludge (CRM144R), and sea water (CASS.4) with satisfactory results. The accuracy was assessed through recovery experiments.

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1. Introduction

Cadmium is considered to be as highly toxic as probably carcinogenic for humans [1]. Cadmium (II) is listed as the sixth most poisonous substance jeopardizing human health. Exposure to lower amounts of cadmium may cause gastrointestinal irritation, vomiting, abdominal pain and diarrhea. Acute exposure may affect kidneys resulting in tubular proteinosis and some times fatality [2].

Different analytical techniques have been reported to determine cadmium ions in water samples including atomic absorption spectrometry [3,4], inductively coupled plasma (ICP)-atomic emission spectrometry and ICP-mass spectrometry [5,6], anodic stripping voltammetry [7,8], differential pulse stripping voltammetry [9,10], potentiometric stripping analysis [11], ion chromatography [12], spectrophotometry [13–15],

electrochemiluminescence [16] and molecular fluorescence spectroscopy [17].

Owing to the co-existence of various heavy metal ions in industrial effluents or other water resources, selective separation of toxic metal ions attracts much attention in both industries and researches. Selective adsorption of an ion on suitable solid sorbent possessing selectivity is inherently attractive to remove of metal ions from dilute aqueous solution [18–20]. Therefore, development a suitable selective solid-phase separator for cadmium (II) in environmental samples is of great significance.

Among the spectral methods, flame atomic absorption spectrometry (FAAS) is simple and rapid for determination of metal ions concentration. However, FAAS is not sensitive to determine Cd(II) at part per billion levels or less. Hence, combining a preconcentration step prior to FAAS determination is often resorted to by various researchers. In addition, in environmental samples, the low concentration of Cd(II) together with the high concentration of other metal ions often requires a preconcentration step combined with a matrix separation. To get a selective solid phase separator, imprinted polymer materials (IPM) have been

* Corresponding author. Tel.: +98 311 3912351; fax: +98 311 3912350.
E-mail address: Ensafi@cc.iut.ac.ir (A.A. Ensafi).

Table 1
SPE preconcentration procedure for cadmium in conjugation with FAAS since 2003

No.	Preconcentration reagent	Solid phase material	pH	Calibration range ($\mu\text{g/L}$)	LOD ($\mu\text{g/L}$)	Enrichment factor	Serious Interferences	Application	Reference
1	5,7-Dibromo-quinoline-8-ol	Benzophenone	6–8	0.1–50	0.1	200	–	Soils, sea and waste water	[2]
2	Diazoaminobenzene (DAAB)	Poly-Cd(II)-DAAB-VP	6	0.21–30	0.21	200	Ca^{2+} , Zn^{2+} , Hg^{2+}	Tap and river water	[22]
3	Bathocuproinedisulfonic acid	Chromosorb-108	8–9.5	20–2000	0.24	80	Al^{3+} , Ag^{+} , Fe^{3+} , Cu^{2+} , Mn^{2+} , Zn^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Pb^{2+}	Tap and river water, wine, rice, tea, honey	[26]
4	1-(2-Pyridylazo)-2-naphthol	Chromosorb-106	8–9	–	0.19	250	Fe^{3+} , Al^{3+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+}	River water, salt, tea, human hair, tobacco	[27]
5	Iodide	Naphthalene-methyltriocetyl ammonium chloride	1.2–10	1–100	0.6	40	–	Tap and Persian gulf water	[28]
6	<i>O,O</i> -Diethyldithiophosphate	Amberlite XAD-4	–	–	1.5	20	Not investigated	Biological samples	[29]
7	2-(6'-Methyl-2'-benzothiazolylazo)chromatropic acid	Polyurethane foam	7.5	10–1000	2.04	22	Fe^{3+}	Natural and tap water, tea, spinach	[30]
8	Chelex-100	Chelex-100	7	–	17	50	Fe^{3+} , Cr^{3+} , Mn^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+}	Sea water reference materials, tea	[31]
9	Diazoaminobenzene-vinylpyridine	Imprinted polymer resin	6	0.21–30	0.21	200	Zn^{2+} , Cu^{2+} , Hg^{2+}	Tap and river water	[32]
10	Co(III) hexamethylenedithiocarbamate	–	6	–	3	100	Ca^{2+} , Mg^{2+} (heavy metals did not study)	Natural water	[32]
11	Methyl thymol blue	Activated carbon	9.0	1–2000	1	1000	–	Natural and tap water, reference materials	Present work

introduced for different metal ions separation [21,22]. However, IPM needs several compounds and long time for the synthesis. Of the various pre-concentration techniques, solid-phase extraction (SPE) has come to forefront in view of several advantages [23]. Table 1 shows a list of the various SPE procedures developed for Cd determination with FAAS, since 2003.

Recently, we have introduced modified activated carbon for highly selective separation and pre-concentration of Pb(II) and Ni(II) [24,25]. In this paper, we describe an on-line column separation and pre-concentration system with FAAS detection for the reliable determination of ultra trace amounts of Cd(II) in environmental samples. The method is based on selective adsorption of Cd(II) ions on an activated carbon modified with MTB, then the adsorbed ions was washed with 0.5 M HNO₃ solution and determined by FAAS. MTB did not wash with the washing solution that was used to remove Cd(II) ions from the column. Automation of the procedure can possibly reduce the risk of operational errors and increase the precision of the method.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade. Doubly distilled water was used throughout.

Activated carbon, 40–60 mesh (Merck, Darmstadt, Germany) was soaked in 6 M hydrochloric acid for 1 day; it was then washed with water and dried at 110 °C for 1 day.

Methyl thymol blue (MTB) solution, 0.010% (w/v), was prepared by dissolving 0.010 g of the reagent (Merck) in water. Samples were filtered through a cellulose membrane of pore size <2 μm.

Universal buffer was made of mixture of acetic acid, boric acid and phosphoric acid (0.04 M).

The following certified reference materials were used: CASS.4 (National Research Council of Canada, Ottawa, Ontario) and CRM 144 R Sewage Sludge from Domestic Origin (Community Bureau of Reference, Brussels, Belgium).

2.2. Apparatus

A Perkin-Elmer (Waltham, Massachusetts, USA), Model 2380 atomic absorption spectrometer furnished with a cadmium hollow-cathode lamp was used. The instrument was set at a wavelength of 228.8 nm and air-acetylene flame was adjusted according to the standard recommendation. The schematic diagram of the on-line pre-concentration system is shown in Fig. 1. The hardware of the system was composed of a 32 channel I/O card, (Advantech, Taipei, Taiwan) Model PCL-720 which has a power relay module to convert the output of I/O card to 220 V ac, a peristaltic pump (Ismatec Model ISM 404 (Glatbrugg, Switzerland)), two 220 V ac electrical valves, a silicon rubber tubing pump (2.06 mm i.d.) and a PC computer, Pentium II (233 MHz). A program was written in Borland C++ by the authors to monitor and to control the system. The mini-column was made by packing Teflon tubes (7.0 mm i.d.) with MTB loaded activated carbon. Small glass wool was plugged at

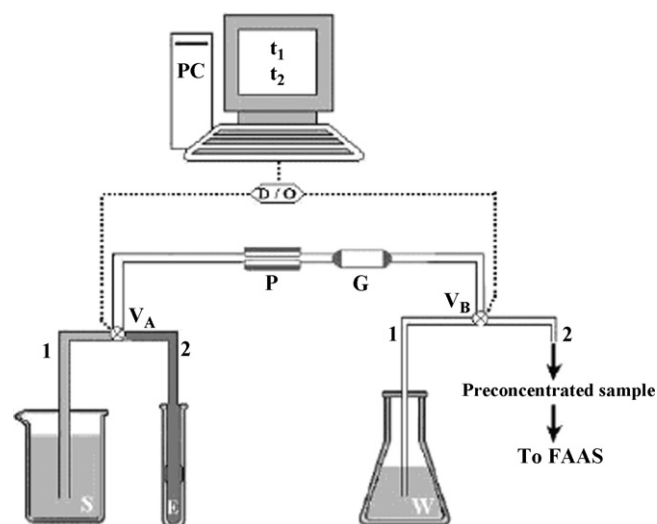


Fig. 1. Automatic manifold system used for pre-concentration of Cd(II). (P, pump; G, microcolumn; D/O, analog to digital converter; S, sample solution; V_A, valve A; V_B, valve B; E, eluent solution (0.5 M HNO₃) and PC, computer).

the end of each column to prevent material loss. A diode array UV–vis spectrophotometer, WPA Lightwave (Cambridge, UK) Model S2000, was used to measure the absorbance of the MTB solution. pH of aqueous solutions was checked using a Metrohm (Herisau AR, Switzerland), Model 827 pH-meter with a glass electrode.

In the on-line pre-concentration procedure, the sample was pumped through the mini-column via position 1 of valve A (Fig. 1). Cadmium (II) ions were retained in the column by forming a complex with MTB. In this case, valve B was in the waste position. When the sample was eluted completely, position 1 of valve A was closed automatically, valve B was switched to the pre-concentration sample and position 2 of valve A was opened when 0.5 M nitric acid was passed through the mini-column to elute the Cd(II) ions by breaking the complex. When the nitric acid was eluted, the pre-concentrated sample was analyzed by flame atomic absorption spectrometer.

2.3. Preparation of modified activated carbon

In a 2000-mL beaker, 10.0 g activated carbon was added to 1.70 g of MTB and mixed well at pH 2.0 (universal buffer, 1.8 L). After 45 h, the mixture was filtered and washed three times with water, each time with 10 mL of water and then dried out. A Teflon column (5.2 cm length and 1.8 cm in diameter) was packed with 0.25 g of the modified activated carbon. The bed height in the column was 1.5 cm.

2.4. Procedure

The method was tested with model solutions before its application to real samples. A 100–1000 mL of Cd(II) solution buffered at pH 9.0, was passed through the column at a flow rate of 3.0 mL/min by opening the position 1 of electrical valves A and B (Fig. 1). After finishing the solution, position 1 of valves A and B is closed automatically, and position 2 of valves A and

B is opened. Therefore, 5.0 mL of 0.5 M nitric acid was passed through the column at a flow rate of 2.0 mL/min to elute the Cd(II) ions. The eluent was collected and analyzed for Cd(II) by flame atomic absorption spectrometry. The percent of the metal ions adsorbed on the column for the known 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 column.

The CASS.4 nearshore seawater reference material for Cd(II) ions was analyzed. The pH of the sample was adjusted to 9 and the solution was passed through the column. Cadmium ions retained on the column were eluted with 5.0 mL of 0.5 M HNO₃ and next introduced into the nebulizer of FAAS as described above.

For Sewage sludge, 80.100 mg of CRM144R Sewage sludge standard reference material sample was decomposed with 16 mL of aqua regia and the solution was evaporated to dryness [31]. This process was repeated twice. To the residue, 10 mL of distilled water was added. The suspension was filtered through a blue band filtering paper and the insoluble residue was washed with distilled water. Next, the above on-line procedure was applied to the final solutions and the blank solution.

3. Results and discussion

Methyl thymol blue (MTB) is a water-soluble metal ion indicator which is used for determination of various metal ions [33]. MTB has used for separation and preconcentration of copper, iron and lead on naphthalene as a solid phase material, at pH 4 [34]. That solid phase has used one time for each sample, and was not reversible. That means that a solution of MTB need for each experiments, and MTB consuming during each separation.

MTB acts as a selective complexing agent for Cd(II) at pH 9.0. On the other hand, we found that this ligand can be adsorbed onto activated carbon. After the adsorption of MTB onto the surface of the activated carbon, it is completely stable and does not wash off when using HNO₃ solution as a washing solvent for Cd(II). This means that the activated carbon treated with MTB solution can be use several times for the separation and preconcentration of cadmium (II) without decreasing the enrichment factor of the solid phase. This may be due to the similarity of MTB structure with activated carbon, producing a strong π - π interaction.

In order to obtain quantitative recoveries of Cd(II) ions on the modified activated carbon, the preconcentration procedure was optimized for various analytical parameters such as pH of adsorption of MTB on the activated carbon, pH of sample solution containing cadmium (II) adsorbed on the column, type, volume and concentration of elution solution, velocity of sample solution through the column, capacity of the modified activated carbon for adsorption of cadmium (II) and influence of sample matrix. In all optimization steps (except for some mentioned steps), 0.25 g activated carbon was used.

For the first of all, we should optimized the variables affect on preparation of the modified activated carbon. To find the best pH for the adsorption of MTB on the activated carbon, different buffer solutions were used. For this purpose, 1.0 mL of 0.010%

Table 2
Influence of pH on adsorption of MTB on activated carbon

pH	λ_{\max}	Absorbance ^a
1.0	438	0.005
2.0	438	0.004
3.0	438	0.016
4.0	438	0.065
5.0	438	0.065
6.0	438	0.080
7.0	438	0.097
8.0	606	0.229
9.0	606	0.375
10.0	606	0.387
11.0	606	0.566

^a Corrected for molar absorption coefficient of MTB at the different pHs.

(w/v) MTB solution was added into a 10-mL volumetric flask, and the solution was diluted to 10 mL with buffer solutions (pH 1.0–11.0). The absorbance of the solution was measured spectrophotometrically at an appropriate wavelength (λ_{\max}) to find the molar absorption coefficient of MTB at the different pHs. Then 15.0 mg of MTB plus 0.10 g activated carbon were mixed in a 100-mL volumetric flask, and the mixture was diluted to 100 mL with buffer solutions (pH 1.0–11.0). After 24 h, the mixture was filtered, and the absorbance of the filtered solution was measured spectrophotometrically. The results are given in Table 2. The results show that the best pH for adsorption of MTB on activated carbon was between 1.0 and 3.0 (Fig. 2). Therefore, a buffer solution of pH 2.0 (universal buffer) was used to prepare the modified activated carbon.

The influence of time on the modification of activated carbon was studied by treating 100 mg activated carbon in the presence of 25.0 mg MTB at pH 2.0 for different times. The results showed that maximum adsorption of MTB on the surface of activated carbon takes places after 45 h (Fig. 3).

The capacity of activated carbon for MTB was also checked. In order to measure the capacity of activated carbon for adsorption of MTB at pH 2.0, 15.0 to 25.0 mg MTB was added into a series of 100-mL volumetric flask and mixed with 0.10 g activated carbon. Then the mixtures were diluted to 100 mL with the buffer solution (pH 2.0). After 45 h, the mixture was filtered and the absorbance of the solution was measured spectrophotometrically. The results are shown in Fig. 4. From the results, we

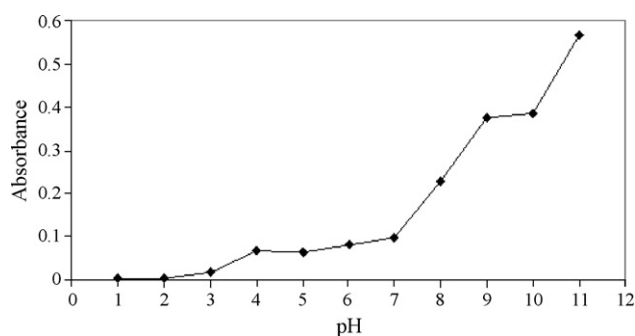


Fig. 2. Influence of pH on the adsorption of MTB on activated carbon. Conditions: 100 mg activated carbon; 15.0 mg MTB; diluted to 100 mL at different pHs (1.0–11.0) mixed and stored for 24 h.

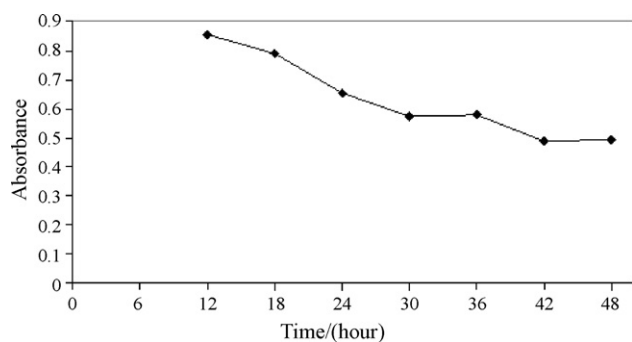


Fig. 3. Influence of time on the modification of activated carbon with MTB. Conditions: 100 mg activated carbon; 25 mg MTB; diluted to 100 mL at pH 2.0.

can calculate that one gram of activated carbon adsorb 170 mg of MTB.

The stability of the adsorbed MTB on activated carbon was checked by elution of the column (containing the modified activated carbon) with 10 mL of 2.0 M HNO₃. The results showed that the ligand did not wash out with 2.0 M nitric acid and it was stable on the surface of activated carbon. The experiment was repeated by washing the column with 5 L of a 0.2 M HNO₃ solution. The results showed that the ligand (MTB) did not wash away during this long-time elution by the mobile phase. In addition, the stability of the modified column was checked after optimization of all experimental variables, using 20 separate solutions (100 mL) of 100 ng mL⁻¹ Cd(II). Cd(II) on those solutions were separated and preconcentrated with the modified column then washed with 5.0 ml of 0.5 M HNO₃ solution and finally analyzed by FAAS. The results showed that the recovery was at least 96.3%. This result shows a good stability of the modified column.

The influence of pH of sample solution on the separation and preconcentration of Cd(II) step was also studied. For this purpose, 100 mL of 50 ng mL⁻¹ Cd(II) at different pH values was passed through the modified solid phase. Then the eluent solution was checked for Cd(II) concentration by FAAS (Fig. 5). The results showed that the most suitable pH range for adsorption of Cd(II) on the modified activated carbon was about 8–10, and that pH 9.0 was the best. This is due to the fact that in acidic solution, the formation constant of the Cd(II)–MTB complex decreases due to the protonation of MTB. Therefore, a universal buffer with pH 9.0 was used for the preconcentration step.

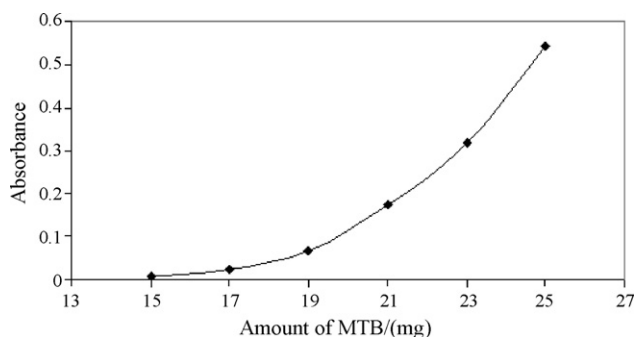


Fig. 4. The capacity of activated carbon for MTB. Conditions: 100 mg activated carbon; diluted to 100 mL at pH 2.0; mixed and stored for 45 h.

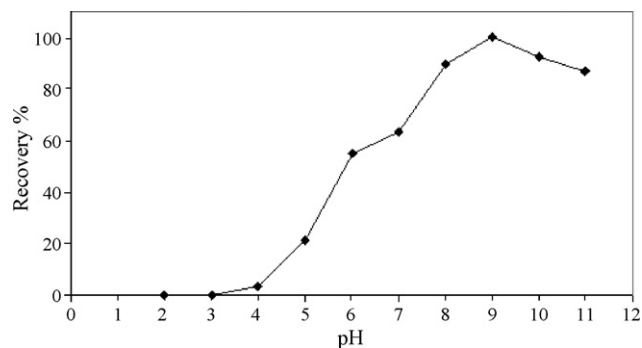


Fig. 5. Influence of pH on adsorption of Cd(II) on the modified activated carbon. Conditions: initial cadmium (II) value, 100 mL of 50 ng mL⁻¹; Washing solution, 5 mL of 0.50 M HNO₃.

Different HNO₃ concentrations (5.0 mL) in the interval range of 0.1 to 1.0 M were tested for the quantitative elution of preconcentrated cadmium (II) ions from the column. The results solution was checked by FAAS to measure the Cd(II) contents. The results showed that 0.5 M HNO₃ is suitable to remove 100% of Cd(II) from the solid sorbent. In order to optimize the volume of 0.5 M HNO₃, 100 mL of 20 ng mL⁻¹ Cd(II) was passed through the modified activated carbon under the optimum conditions. Then the solid phase was washed with different volumes of 0.5 M HNO₃ (2–10 mL). The results showed that 2 mL 0.5 M HNO₃ is suitable to remove 100 ± 1.4% of Cd(II) from the solid phase. Therefore, 2 mL of 0.5 M HNO₃ was used as a washing solution to remove total Cd(II) ions from the column.

The influence of the sample flow rate for adsorption of cadmium (II) to the column was also investigated. For this purpose, 100 mL of 20 ng mL⁻¹ Cd(II) solutions was passed through the modified column at various flow rates between 1 and 9 mL/min. Then the adsorbed cadmium (II) was washed with 5 mL of a 0.5 M HNO₃ solution. Then the cadmium (II) content was measured with FAAS. The results showed that increasing the flow rate of sample solution up to 3 mL/min did not affect the recovery of Cd(II) from the modified activated carbon, and the recovery was 100 ± 1.2%. Therefore, a sample flow rate of 3 mL/min was used for further study.

The effect of the eluent flow rate (HNO₃, 0.5 M) was also checked in the range of 1–5 mL/min. The results showed that the recovery of cadmium was maximized when using elution rates up to 2 mL/min.

The capacity of the modified activated carbon for adsorption of Cd(II) was checked by passing a series of 100 mL solutions containing 5–50 µg Cd(II) through the column (containing 0.25 g modified activated carbon). From the results, we found that the capacity of the solid adsorbent is equal to 80 µg of cadmium per 1 g of the modified activated carbon.

The influence of matrix ions in water samples on the recovery of cadmium (II) ions with the system was also investigated by passing different amounts of potential interfering ions plus 20.0 ng mL⁻¹ Cd(II). Tolerable amounts of foreign ions, giving less than 5% error in the cadmium determination, were evaluated. The results are given in Table 3.

The method was used for different samples for Cd(II) determination: Zayandeh Roud river water (Isfahan), tap water, and

Table 3

Effect of the matrix ions on the solid phase selectivity on separation and pre-concentration of 20.0 ng/mL Cd(II)

Metal ion	Tolerance ratio ($W_{\text{ion}}/W_{\text{Cd(II)}}$)
Pb ²⁺ , Fe ²⁺ , Sn ²⁺ , Na ⁺ , Ca ²⁺ , K ⁺ , NO ₃ ⁻ , CH ₃ COO ⁻ , BO ₃ ³⁻ , PO ₄ ³⁻ , Mg ²⁺ Hg ²⁺ , Mn ²⁺ , Zn ²⁺ , Ni ²⁺ , Co ²⁺ Cu ²⁺	1000 ^a 500 250

^a Maximum concentration of ion tested. Hundred milliliter of 20 ng/mL Cd(II) ions were used.

Table 4

Determination of Cd(II) in water samples

Sample	Cd(II) added (ng/mL)	Cd(II) found ($n=4$) (ng/mL)	Recovery (%)
Tap water	–	4.4 ± 0.4	–
	10.0	14.2 ± 0.3	99.0
	20.0	23.8 ± 0.5	98.0
	30.0	34.8 ± 0.6	101.0
Zayandeh Roud river water	–	2.1 ± 0.2	–
	10.0	12.0 ± 0.2	99.0
	20.0	22.4 ± 0.4	101.0
	30.0	31.1 ± 0.7	97.0
CASS-4 nearshore seawater reference material ^a	–	<DL	–
	10.0	10.1 ± 0.1	101.0
	20.0	19.9 ± 0.2	99.5
** CRM-144R	–	1.87 ± 0.1 μg/g	–

** Certified value: 1.84 μg/g.

^a Certified value: 0.026 ± 0.003 μg/L; <DL: below the detection limit.

the following reference materials: sewage sludge (CRM-144R), and sea water (CASS-4). The river water samples were directly measured by the proposed method after filtering with a filter paper (Schleicher & Schuell® no. 589³, Blue ribbon). For each sample, 250 mL was passed through the column as explained by the recommended procedure. Then the cadmium (II) contents in the washed solution were determined by FAAS. CASS-4 reference material was spiked with various amounts of cadmium (II) to obtain the concentration of Cd(II). After that, cadmium (II) was determined using the on-line separation/preconcentration system. The results are given in Table 4. There was a good agreement between the added and the recovered amount of the analytes.

4. Conclusions

The new developed method is both a selective and a repeatable method for separation, preconcentration and determination of ultra trace amounts of cadmium (II). The modified activated carbon phase is stable for several treatments of sample solutions without the need for using any chemical reagents. The method can be used for preconcentration of cadmium (II) down to 0.001 μg mL⁻¹. Under the optimum conditions, cadmium in aqueous samples was concentrated about 1000-fold. The relative standard deviations for 10 independent determinations reached

values of 4.2, 4.0 and 3.0% for solutions of 20.0, 50.0 and 100.0 ng mL⁻¹ Cd(II), respectively. The obtained results are in good agreement with the certified values, which proved the applicability of the presented method to the quantitative separation/preconcentration of cadmium in the sediment and sewage sludge samples. The recovery of spiked cadmium (II) was in the range of 97–101%. If the selectivity of the proposed method is compared with the previously published papers, it is obviously seen that this method has higher selectivity toward Cd(II).

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