

Preconcentration and determination of cadmium in some samples using solid phase extraction with slotted quartz tube flame atomic absorption spectrometry

Y. Arslan¹, D. Trak², E. Kendüzler^{2*}

¹Mehmet Akif Ersoy University, Faculty of Arts & Sciences, Nanoscience and Nanotechnology Department, 15030 Burdur, Turkey

²Mehmet Akif Ersoy University, Faculty of Arts & Sciences, Chemistry Department, 15030 Burdur, Turkey

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In this study, a two-step preconcentration method is proposed for the determination of trace amounts of Cd(II). In the first preconcentration step, Amberlite CG-120 resin was used. After the separation and preconcentration of Cd(II), a slotted quartz tube was used for its FAAS determination. In this part, the slotted quartz tube was used as the second preconcentration step. Some experimental parameters influencing the separation and preconcentration of Cd(II) were separately optimized. The total enrichment factor was found to be 920 after the two steps of preconcentration and the detection limit was found to be 0.1 µg/L. Accuracy of the method was checked by analysing a standard reference material (Environmental Matrix Reference Material, Lake Water, TMDA-70.2). The proposed two-step preconcentration method was applied to the analysis of drinking water.

Keywords: cadmium; solid phase extraction; two-step preconcentration method; Amberlite CG-120 resin; slotted quartz tube; flame atomic absorption spectrometry.

INTRODUCTION

Elevated heavy metal concentrations in the atmosphere are caused by serious pollution from the industrialization activities [1]. The Environmental Protection Agency (EPA) proposed that cadmium is among thirteen toxic metal species in the priority pollutant list [2]. Cd is one of the most toxic elements for living organisms and it shows severe unwanted effects, especially on kidneys [3]. The half-life of Cd in the kidney is about 30 years. Therefore, the determination of Cd in different samples is very significant for food and environmental control [4].

Flame atomic absorption spectrometry (FAAS) [5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6], inductively coupled plasma mass spectrometry (ICP-MS) [7], cold vapor generation atomic absorption spectrometry (CVG AAS) [8], graphite furnace atomic absorption spectrometry (GF-AAS) [9] and electrothermal atomic absorption spectrometry (ETAAS) [10] are the most proper techniques for the determination of Cd(II) with different sensitivity. Among the above techniques, FAAS has been the commonly preferred technique for the determination of some heavy metals at trace levels. However, the sensitivity of FAAS is inadequate for direct trace analysis. Preconcentration and/or separation methods are

often required before the FAAS analysis at trace levels [11].

There are several methods used for preconcentration and separation of Cd(II), such as solid-phase extraction (SPE) [12], non-dispersive ionic liquid based microextraction (NDILME) [13], multi-step cloud point extraction procedure (CPE) [14] and dispersive solid-phase extraction (DSPE) [10]. Among them, the SPE has been frequently used for the preconcentration and separation of elements from some matrices because of its simplicity, speed, low cost, and low consumption of reagents [15].

In recent years, ionic imprinted polymers (IIPs) [16], multiwalled carbon nanotubes (MWCNTs) [17], modified polyurethane foam [18] and modified silica gel [19] have been used for the preconcentration and separation of Cd(II) in some matrices prior to its determination.

Additionally, there have been various applications to improve FAAS sensitivity in the detection step. One of the preferred devices called slotted quartz tube (SQT) was developed by Watling in 1977. Using the SQT device the sensitivity of FAAS has been increased from 2 to 5 fold depending on the element [20]. In the literature, there are some studies on the determination of metals at trace levels using the SQT-FAAS [21-23].

In this work, Cd(II) was enriched by a two-step preconcentration method. Amberlite CG-120 was employed as the adsorbent for the separation and preconcentration of Cd(II) (first preconcentration step). The functional groups of this resin are Na⁺

* To whom all correspondence should be sent:

E-mail: kenduzler@mehmetakif.edu.tr

form and sulfonic acid groups. The optimum pH values of this resin are in the range of ~0.4-10 [24]. In the first preconcentration step, some experimental parameters, such as pH, amount of adsorbent, sample volume and flow rate, eluent volume and flow rate for quantitative recovery of Cd(II) were optimized to obtain the best separation and/or preconcentration conditions. Furthermore, the SQT device was used together with the FAAS to further enhance the sensitivity of the system (second preconcentration step). The developed two-step preconcentration method (SPE and SQT device) was applied for the determination of Cd(II) in drinking water.

EXPERIMENTAL

Apparatus

In this study, the ATI UNICAM 939 model FAAS was used equipped with a deuterium lamp as background corrector, a Cd hollow-cathode lamp as light source (current, 8.0 mA; wavelength, 228.8 nm; bandwidth of the slit, 0.5 nm), acetylene flow rate, 1.1 L/min, slotted quartz tube with two slots (length of slotted quartz tube, 12 cm; length of top slot, 4 cm; length of lower slot, 5 cm). The pH values were controlled with a Thermo Orion 3 Stars Model pH meter.

Reagents

All chemicals were of analytical reagent grade and 18 M Ω .cm deionized water from a PURIS purification system (Model: Expe-UP Series) was used for the preparation of solutions. All glass vessels were cleaned before usage by soaking in 5% HNO₃ and then rinsed thoroughly with deionized water. 65% (w/w) HNO₃ and 60% (w/w) HClO₄ were obtained from Merck. 37% (w/w) HCl, was obtained from Riedel-de Haen.

Preparation of Cd(II) solution

Cd(NO₃)₂·4H₂O was supplied from Aldrich and a 1000 mg/L stock solution of Cd(II) was prepared by dissolving 0.280 g of Cd(NO₃)₂·4H₂O in 100 mL of deionized water. Working solutions of Cd(II) were prepared from the stock solution by dilution.

Column preparation

The glass column used in this study has 15 cm in length and 0.8 cm in internal diameter. In the preparation step of the column, a small glass wool wad was placed at the bottom of the column and 300 mg of Amberlite CG-120 resin was added on it. Afterwards, another small glass wool wad was

inserted onto the top of the resin. Before use, the Amberlite CG-120 resin in the column was washed consecutively with ethanol, 1 mol/L HCl, 1 mol/L HNO₃, and water. After each usage, the column was filled with deionized water and stored until the next experiment.

General procedure for the sorption of Cd(II) on the column

The column was firstly preconditioned at pH 1 using both 1 and 10% (w/w) HCl. 25 mL of a model solution containing 5 μ g of Cd(II) was adjusted to pH 1 using both 1 and 10% (w/w) HCl. Then, the model solution was passed through the column at a flow rate of 5 mL/min. The adsorbed Cd(II) ions on the column were eluted with 5 mL of 3 mol/L HNO₃ at a flow rate of 1 mL/min. The eluent solution was analyzed by FAAS. The column filled with Amberlite CG-120 resin was used repeatedly after washing it with 10 mL of 3 mol/L HNO₃ solution and amply with deionized water.

Collection and preparation of samples

The developed two-step preconcentration method was applied to determine Cd(II) in drinking water. Commercial natural drinking waters were purchased from the local market in Burdur city, Turkey.

RESULTS AND DISCUSSION

In this study, Cd(II) was enriched by a two-step preconcentration method. Some experimental parameters of the first step, such as pH, amount of sorbent, concentration and type of eluent, sample and eluent flow rate, and sample volume were optimized. Then, some parameters of the second step using a SQT device, such as observation height (distance between the top of burner head and SQT device) and acetylene flow rate were optimized.

Effect of pH

pH is an important analytical parameter in the solid phase extraction of metal ions. In this study, the recovery values on the Amberlite CG-120 resin were determined at different pH values in the range of 1-5. As seen in Fig. 1, quantitative recovery of Cd(II) was obtained for all pH values in the range. pH 1 was chosen as the optimum pH value.

Effect of the amount of Amberlite CG-120 resin

The effect of the amount of Amberlite CG-120 resin is another significant parameter for an efficient extraction procedure. Different amounts of

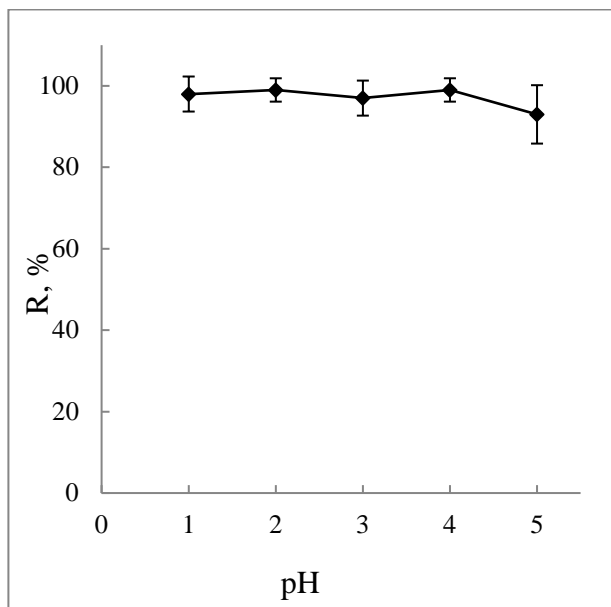


Fig. 1. Effect of pH on the recovery of Cd(II) on a column of Amberlite CG-120.

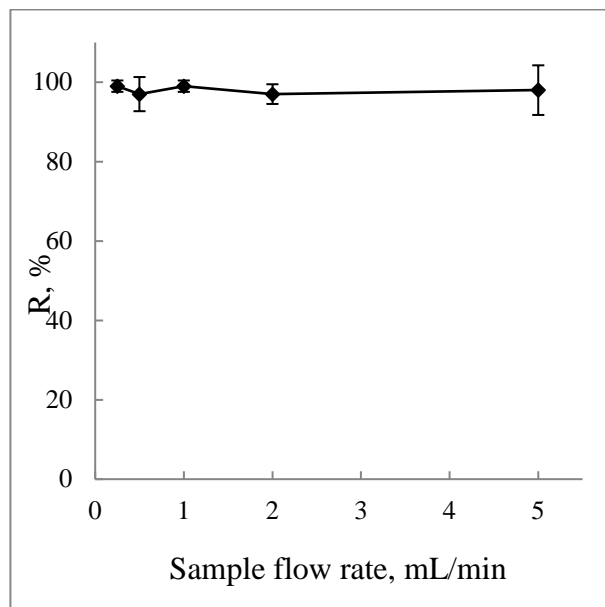


Fig. 2. The effect of sample flow rate on the recovery of Cd(II) on a column of Amberlite CG-120.

Amberlite CG-120 resin in the range from 0 to 500 mg were used and quantitative recoveries were obtained with 100 to 500 mg of Amberlite CG-120 resin. For quantitative recovery in the case of real samples, 300 mg of Amberlite CG-120 resin were used in further experiments.

Effect of type and volume of eluent

A series of eluent solutions, viz. 2 mol/L HNO₃, 2 mol/L HCl, 2 mol/L HClO₄ and ethanol, were employed in order to find out the suitable eluent type and volume. Quantitative recovery of Cd(II) was achieved with 10 mL of 2 mol/L HCl. After that, the optimum concentration and volume of HCl were optimized. To this purpose, various concentrations of HCl between 0.1 and 4.0 mol/L and volumes of 5 and 10 mL of HCl were taken. It was found that quantitative elution is achieved by using 5 mL of 3 mol/L HCl. Therefore, 5 mL of 3 mol/L HCl solution was employed in all studies.

Effect of flow rate of sample and eluent solution

The sample flow rate through the column is a substantial factor which influences both the recovery of analyte and the time of analysis. Thus, the flow rates of sample and eluent solution were investigated. The model solution was passed through the column at a flow rate changing from 0.25 to 5 mL/min. Quantitative recovery was obtained for all sample flow rates shown in Fig. 2 and 5 mL/min was chosen in order to shorten the analysis time. The eluent solution was passed through the Amberlite CG-120 resin at flow rates ranging from 0.25 to 2 mL/min. With all eluent

flow rates, quantitative recovery was achieved and 2 mL/min was selected to shorten the analysis time.

Effect of sample volume

For determining the enrichment factor of Cd(II), volumes of 25, 50, 100, 250, 500, 750 and 1000 mL of sample solution containing 5 µg Cd(II) were passed through the Amberlite CG-120 resin. The recovery of Cd(II) was quantitative for all sample volumes, as shown in Fig. 3.

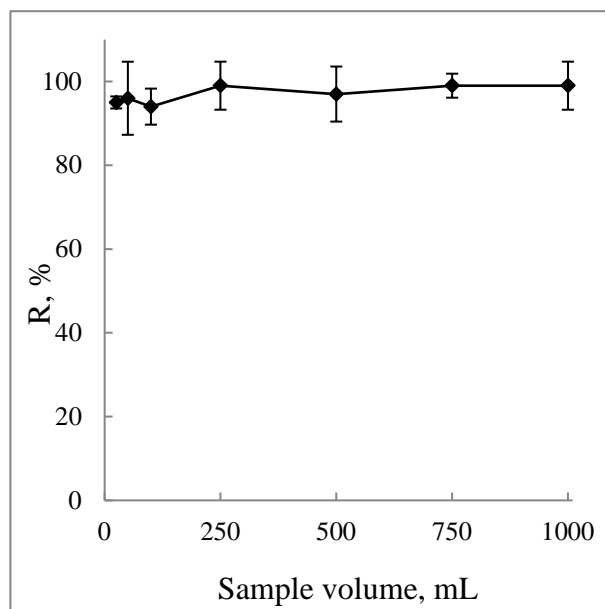


Fig. 3. Effect of sample volume on the recovery of Cd(II) on a column of Amberlite CG-120.

1000 mL was chosen as the optimum sample volume; and the eluent volume was chosen as 5 mL. In this way a preconcentration factor of 200 was achieved in the first preconcentration step of this proposed study.

Slotted Quartz Tube (SQT) optimizations

FAAS equipped with a SQT device was used for further improving sensitivity (second preconcentration step). The important parameters here - acetylene flow rate and observation height were optimized. The proper acetylene flow rate was identified as varying from 0.8 L/min to 1.4 L/min. At 1.1 mL/min acetylene flow rate, the maximum peak area for Cd(II) was obtained. The effect of the observation height on the Cd(II) signal in the range from 0.6 to 0.8 cm was studied. The optimum observation height was found to be 0.7 cm.

Matrix effects

Matrix effects should be investigated since accompanying ions present in the real samples may affect the analyte signal positively and/or negatively. For this, different cations prepared from salts with Cl⁻, NO₃⁻, SO₄²⁻ ions were added individually to the model solution of Cd(II) and then the proposed preconcentration method was applied. The results are given in Table 1. As can be seen, the proposed method is independent of matrix effects at the working concentrations of the selected elements.

Analytical figures of merit

In the proposed study, the equations of the calibration plots for FAAS and SQT-FAAS were found as $y=0.0682x+0.0004$ and $y=0.3156x+0.0076$, respectively. The comparison of the slopes of the calibration plots without and with SQT device yielded a 4.6-fold enrichment. In addition, using the Amberlite CG-120 resin, a 200-fold enrichment was

obtained. The total enrichment factor for Cd(II) determination using the two-step preconcentration method was found to be 920.

The limit of detection (LOD) was calculated using both Amberlite CG-120 resin and SQT device. For this reason, 25 mL of model solution containing 0.5 µg Cd(II) was passed through the Amberlite CG-120 resin. The retained Cd(II) on the Amberlite CG-120 resin was eluted by 25 mL of 3 mol/L HNO₃. Then, the eluent was used for the determination of LOD (3s). LOD was found to be 0.1 µg/L by the two-step preconcentration method (N=11).

Accuracy and analytical application

The accuracy of the method was evaluated by the determination of Cd(II) in the standard reference material, Environmental Matrix Reference Material, Lake Water, TMDA-70.2. The column was firstly preconditioned at pH 1.0. Then, 25 mL of standard reference material was adjusted to pH 1.0 and passed through the column. The elution of Cd(II) from the resin was performed using 3 mol/L HNO₃. Then the eluent solution was analyzed using the SQT-FAAS method. Cd(II) concentration in the standard reference material was found to be 142±8 µg/L with a relative error of 1.4% based on four replicate measurements at the 95% confidence level, which is a good agreement with the certified value of 140±9 µg/L. Therefore, it seems that the proposed two-step preconcentration method is useful for the preconcentration of trace levels of Cd(II) in the presence of other metal ions which shows the applicability of the method.

The proposed two-step preconcentration method was also applied for the determination of Cd(II) in drinking water and the accuracy of the method was checked by the determination of the recovery of spiked Cd(II) in the drinking water, as shown in Table 2.

Table 1. Effect of some ions on the recovery of Cd(II).

Ion	Concentration (mg/L)	R* (%)	Ion	Concentration (mg/L)	R* (%)
Na ⁺	1	98±5	Cu ²⁺	1	97±4
	5	95±4		5	96±3
	50	95±3		50	93±1
K ⁺	1	98±2	Mn ²⁺	1	96±2
	5	95±2		5	98±4
	50	96±3		50	100±3
Mg ²⁺	1	100±4	Al ³⁺	1	93±3
	5	97±6		5	93±2
	50	101±6		50	96±1
Fe ³⁺	1	100±1	Co ²⁺	1	94±2
	5	97±5		5	95±1
	50	92±1		50	94±5

* $\bar{x} \pm s$, (N=3)

Table 2. Determination of Cd(II) in drinking water (N=3).

Added Cd(II), µg/L	Found, $\bar{x} \pm \frac{ts}{\sqrt{N}}$ µg/L	Relative error, %
-	N.D. ^a	-
10	9.6±1.7	-4
20	20.2±1.5	+1

^a N.D.: Not detected**Table 3.** Determination of Cd(II) in drinking water (N=3).

Study	pH	EF ^a	Resin type	Sample volume, mL	Measuring instrument	LOD, µg/L	Ref.
1	4.8	160	Duolite XAD-761 resin	800	FAAS	0.38	[25]
2	8	250	Mini-column packed with sulfur	500	FAAS	0.2	[26]
3	6	282	Multiwalled carbon nanotubes/poly(2-amino thiophenol) nanocomposites	2200	FAAS	0.3	[27]
4	8.5	80	Column packed with sulfur powder modified with 2-mercaptobenzothiazole	200	CVG-AAS	4.6.10 ⁻³	[8]
This study	1	920	Amberlite CG-120	1000	SQT-FAAS	0.1	-

CONCLUSIONS

In conclusion, the suggested two-step procentration method (solid-phase extraction with Amberlite CG-120 resin and SQT) is a rapid, simple, economic, accurate and precise method for the preconcentration and determination of Cd(II) in different environmental samples. This method possesses several advantages. For example, there is no necessity of using buffer and chelating agents for the separation and preconcentration of Cd(II). The method has a high enhancement factor, high tolerance limit for matrix ions, low detection limit and works in a strongly acidic medium. The analytical performance of the proposed method is compared with that of other preconcentration methods in the literature, as shown in Table 3.

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ПРЕ-КОНЦЕНТРИРАНЕ И ОПРЕДЕЛЯНЕ НА КАДМИЙ В НЯКОИ ПРОБИ ЧРЕЗ ТВЪРДО-ФАЗНА ЕКСТРАКЦИЯ И ПЛАМЪКОВА АТОМНО-АБСОРБЦИОННА СПЕКТРОФОТОМЕТРИЯ (FAAS)

Я. Арслан¹, Д. Трак², Е. Кендюзлер^{2*}

1 Университет „Мехмет Акиф Ерсой“ Факултет за изкуства и наука, Департамент по нанонауки и нанотехнологии, 15030 Бурдур, Турция

2 Университет „Мехмет Акиф Ерсой“, Факултет за изкуства и наука, Департамент по химия, 15030 Бурдур, Турция

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(Резюме)

В тази работа се предлага дву-степенно пре-концентриране с определянето на след от Cd(II). За първото пре-концентриране се използва йонообменна смола Amberlite CG-120. След разделянето и пре-концентрирането кадмият се определя чрез FAAS в тясна кварцова кювета. Кюветата се използва за вто пре-концентриране. Отделно са оптимизирани някои експериментални параметри влияещи на пре-концентрирането и разделянето на Cd(II). Факторът на обогатяване е определен на 920 след две степени на пре-концентрация, а границите на откриване са 0.1 µg/L. Точността на метода е проверена чрез анализа на стандартни референтни материали (Environmental Matrix Reference Material, Lake Water, TMDA-70.2). Предложената дву-степенна процедура е приложена за анализа на питейна вода.