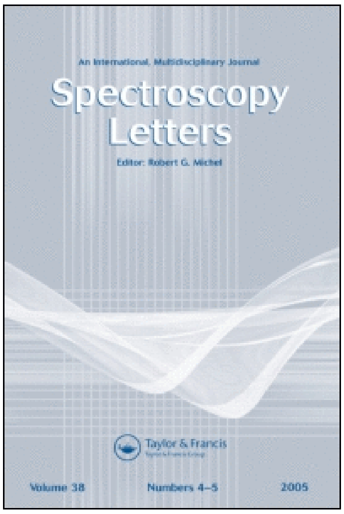

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Online Preconcentration/Determination of Cadmium Using Grape Bagasse in a Flow System Coupled to Thermospray Flame Furnace Atomic Absorption Spectrometry

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Abstract: Thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) was employed for Cd(II) determination after online preconcentration. In this system, Cd(II) ions were adsorbed onto a minicolumn packed with grape bagasse. The elution of the metal ions was made with 1 mol L^{-1} HCl. Various parameters, such as pH, eluent type, concentration, volume, flow rate for preconcentration, and effect of interfering ions on the retention of the metal ions have been studied. The optimum pH for the adsorption was 3.0. The enrichment factor was 33.7. The limits of detection and quantification for Cd(II) were 0.03 and 0.11 $\mu g\,L^{-1}$, respectively. The repetitivity and precision were 5.0 (5 minicolumns) and 4.6% (n = 18). The stability of the minicolumns was evaluated from successive preconcentration/elution cycles (80 cycles, RSD 3.9%). The proposed method was applied for cadmium determination from certified reference materials, and good agreement was obtained at the 95% confidence level.

Keywords: Cadmium, grape bagasse, preconcentration, thermospray

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INTRODUCTION

The determination of metals at low concentration levels in environmental samples requires the use of sensitive techniques. Electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma–mass spectrometry (ICP-MS) have been employed for this task. Additionally, flame atomic absorption spectrometry (FAAS) can also be used, mainly when preconcentration procedures are also used if requirements related to instrumentation, maintenance, and acquisition costs are important.[1]

A variety of methods can be employed for the preconcentration and/or separation of metal ions, including ion exchange, cloud point extraction, solvent extraction, and others.[2–4] Solid-phase extraction is one of the most rapid and economic preconcentration methods for many different samples, including environmental, biological, and so forth. For this purpose, some solid-phase extractants, including activated carbon, resins, polyurethane foam, and other materials, have been used.[5,6] Recently, biological materials (algae, fungi, bacteria) or certain waste products from industrial or agricultural activities have been used as adsorbents for metal remediation.[7–9] Studies to access the ability of natural materials, such as apple residue,[10] vermicompost,[11] rice husks,[12] and others, for metal adsorption have also been proposed. These adsorbents, when compared with synthetic materials, have some advantages, such as low cost, natural abundance good adsorption capacity, and so forth. [13,12] This last property can be attributed to the presence of carboxyl, hydroxyl, sulfate, phosphate, and amino groups in the natural materials.[14]

These characteristics can be reinforced when online systems are considered for metal preconcentration using natural adsorbents followed by FAAS. Flow systems are excellent sample managers, as they can significantly reduce the risks of sample contamination (an essential prerequisite for trace analysis). Other relevant characteristics can also be found in the literature, mainly when these systems are coupled to atomic spectrometry.[15–17] However, even when coupling online preconcentration systems to FAAS, the limits of detection may not be sufficiently low to permit trace metal analysis. As the inherent conception of thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) is to achieve lower limits of detection, due to its good nebulization efficiency, the coupling of online preconcentration systems to TS-FF-AAS can reinforce the previously indicated good analytical characteristics. Some examples in the literature demonstrate such characteristics.[18–20]

The current work points out a mechanized system based on the flow injection concept for online cadmium preconcentration and subsequent determination by TS-FF-AAS, using a by-product (grape bagasse) from wine production as a natural adsorbent material. Cadmium ions retained in the material were eluted with HCl. The influence of pH, concentration and volume of eluent, and preconcentration flow rate were investigated. The accuracy of the presented method was assessed using three certified reference materials (BCR-

281, trace elements in rye grass; BCR-189, trace elements in whole-meal flour; and BCR-191, trace elements in lyophilized brown bread).

MATERIALS AND METHODS

Instrumentation

The measurements were carried out using a Perkin-Elmer model AAnalyst 300 flame atomic absorption spectrometer equipped with deuterium lamp background correction and a cadmium electrodeless discharge lamp (Perkin-Elmer Co., Norwalk, CT, USA). The operating conditions were those recommended by the manufacturer.

A Digimed DM20 pH meter (Digimed Instrumentação Analítica Ltda., São Paulo, Brasil) was used to adjust the pH of the solutions. A Provecto Analítica microwave oven, model DGT100 Plus (Provecto Analítica Ltda, Jundiaí, Brazil) was employed for microwave-assisted decomposition of the certified reference materials. The preconcentration system included a homemade injector-commutator to select preconcentration/elution steps. An Ismatec model IPC peristaltic pump (Ismatec SA, Zurich, Switzerland) with Tygon tubes and a confluence point built from Teflon were also used.

Reagents and Material

Grape bagasses, a by-product from wine production (Brazil), were dried in an oven at 40°C to constant mass and sieved to obtain particle sizes between 75 and 355 μm for the adsorption tests. Afterwards, the grape bagasses were stored in polyethylene flasks and used without any further physical or chemical treatment.

All chemicals used in this study were of analytical grade. Deionized water (18.2 MΩ cm) obtained from a Milli-Q system (Millipore Co., Bedford, MA, USA) was used to prepare all solutions. Cadmium stock solution of 1000 mg L^{-1} (Hexis Científica Ltda, Jundiaí, Brazil) was used. Further working solutions were freshly prepared from the stock solution for each experimental run. Hydrochloric and nitric acid solutions were prepared by appropriate dilution (Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA). Phosphate (KH_2PO_4/NaOH 0.1 mol L^{-1}) and 0.1 mol L^{-1} hydrogenphthalate (in 0.1 mol L^{-1} HCl or NaOH) buffer solutions were used to adjust the pH.

TS-FF-AAS System

The TS-FF-AAS system comprises a nickel tube 10-cm long with 10-mm i.d. that is positioned on a standard burner head (by means of a stainless steel support) and a ceramic capillary (0.5 mm i.d. and 10 cm long). The nickel tube has six holes of 2-mm diameter at the bottom, into which flame gases enter the tube, and a hole 90 degrees to the bottom where the ceramic capillary is introduced. This capillary is used for introducing sample into the nickel tube.

Minicolumn and Online Preconcentration System

The minicolumn used for preconcentration of cadmium was prepared by packing 100 mg of grape bagasse into pipette tips (used in automatic micropipette) with capacity for 200 μL. A small amount of glass wool was placed on the top and at the tip of the minicolumn to prevent possible adsorbent loss during the preconcentration/elution processes. The minicolumn was connected to a peristaltic pump through Tygon tubes. A diagram of the minicolumn and the online preconcentration system is shown in Fig. 1. This system is based on the introduction of a solution containing the metallic species, using a peristaltic pump, into the minicolumn for a specific period of time, while the carrier (water) is continuously pumped to the TS-FF-AAS system. The metal retained on the adsorbent is then eluted with an acid solution and flows toward the nickel tube.

Before use, a 1.0 mol L^{-1} hydrochloric acid solution and deionized water pass through the minicolumn for cleaning and conditioning. The entire cycle consists of the preconcentration and elution steps. In the preconcentration step, the sample is percolated through the minicolumn at an appropriate pH (adjusted with buffer solution) for 4 min at 1.0 mL min^{-1}. At the same time, a nitric or hydrochloric acid solution fills the eluent loop, while water is pumped at a 0.6 mL min^{-1} flow rate to the nickel tube. The injector commutator is then manually changed to the elution position and a fixed volume of acid solution passes through the minicolumn, in the opposite direction, eluting the analytes. They are eluted at 0.6 mL min^{-1} directly to the ceramic capillary

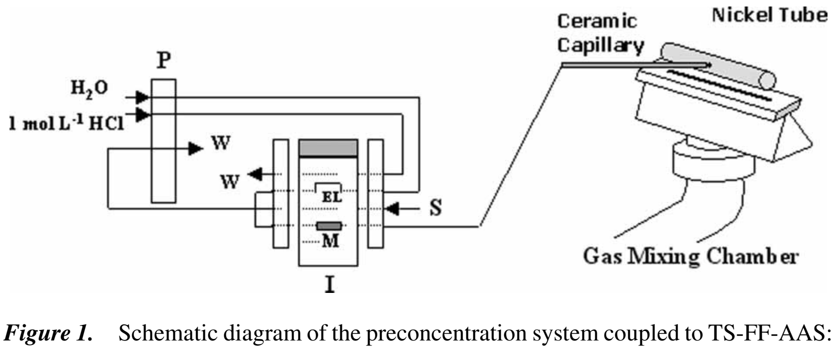

Figure 1. Schematic diagram of the preconcentration system coupled to TS-FF-AAS: elution position. P, peristaltic pump; I, injector commutator; W, waste; S, sample; M, minicolumn; EL, eluent loop.

and the nickel tube, where the thermospray is formed. Working solutions and blanks were submitted to the same preconcentration procedure.

The use of buffer solution is an alternative to guarantee an optimum adsorption pH for every preconcentration cycle, as an acid solution is used in the elution step.

The system was optimized by varying the chemical and flow conditions using the univariate method, searching for higher absorbance. The preconcentration procedure was optimized for some parameters, such as pH, eluent type, concentration and volume of eluent, preconcentration flow rate, and the effect of interfering ions.

Sample Preparation

The following certified reference materials were analyzed: BCR-281 (trace elements in rye grass), BCR-189 (trace elements in whole-meal flour), and BCR-191 (trace elements in lyophilized brown bread). For their decomposition, ca. 300 mg of material was treated with 10 mL conc. HNO_3 and 2 mL of 30% (v/v) H_2O_2 in a closed vessel of a microwave oven. The program used consisted of three steps: 400 W for 5 min, 700 W for 5 min, and 0 W for 3 min. After digestion, the resulting solutions were heated on a hot plate almost to dryness. After cooling, the pH of the samples (initial pH at 1) were adjusted with a buffer solution (hydrogenphthalate/0.1 mol L^{-1} HCl) for pH 3 and transferred to 25-mL calibrated flasks. Blank solutions were similarly prepared. These samples were submitted to the proposed method for Cd(II) determination.

RESULTS AND DISCUSSION

Effect of pH and Eluent Type

The effect of pH on cadmium retention was investigated. For this purpose, the solution pH was adjusted to a fixed value in the 2–8 range using appropriate buffers (from 2 to 6 using hydrogenphthalate/HCl or NaOH and from 6 to 8 using KH_2PO_4/NaOH). These solutions were passed through the minicolumn at 1.0 mL min^{-1} for 4 min. Nitric and hydrochloric acids were chosen as eluent, owing an effective elution of the adsorbed metal. After elution, the cadmium was determined by the TS-FF-AAS system. According to the results shown in Fig. 2, the maximum retention for cadmium occurred at pH 3.0.

The results clearly show that metal adsorption depended on pH. At low pH values, there is a possible competition between H^+ and metal ions for the same metal binding sites of the adsorbent. The material surface becomes more positively charged at low pH values, decreasing the attraction between metal ions and the functional groups of the grape bagasse. For pH values higher than

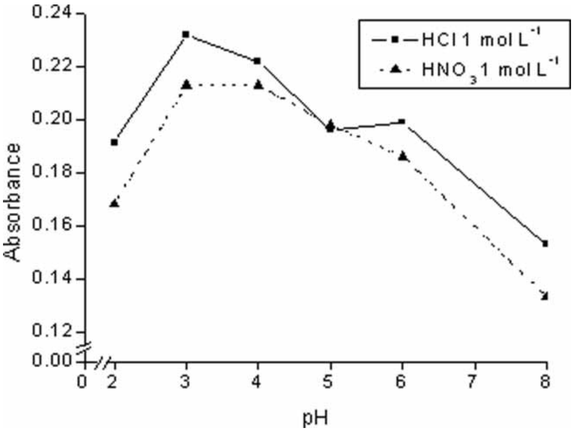

Figure 2. Effect of solution pH (buffer solution) on the absorbance using 1.0 μg L^{-1} Cd(II): sample volume, 4 mL; eluent, 250 μL of 1.0 mol L^{-1} nitric or hydrochloric acid; ■, HCl; ▲, HNO_3.

3.0, the retention decreases again because of the formation of hydroxylated complexes with the metal ions.[21] These results show that the adsorption could be attributed to ionic attraction between the metal ion and the adsorbent.

Lower pH values are generally preferred for analyzing samples (biological, geological, etc.), because these samples undergo acid digestion and precipitation or hydrolysis of metallic analytes are avoided. For subsequent experiments, a pH value of 3.0 was used.

Nitric and hydrochloric acids were tested for eluting the metal from the minicolumn (Fig. 2). Elution using nitric acid was less satisfactory because lower detectability (ca. 10%) was observed. Thus, hydrochloric acid was used as eluent in subsequent experiments.

Effect of the Eluent Concentration and Volume

Another important factor that affects the preconcentration system is eluent concentration for releasing the metal ion from the grape bagasse. Different concentrations of hydrochloric acid (from 0.05 to 1.50 mol L^{-1}) were tested. The effect of the eluent concentration on the cadmium absorbance signal is shown in Fig. 3. As can be seen, the signal increased up to 1.0 mol L^{-1} HCl concentration and then remained constant. The concentration of the acid used as eluent must be as low as possible in order to prevent adsorbent degradation. Then, 1.0 mol L^{-1} HCl acid was selected for subsequent studies.

The quantity of acid that passes through the minicolumn is a function of eluent loop volume (EL; Fig. 1). The influence of this parameter on metal preconcentration is shown in Fig. 4. The maximum signal was found using

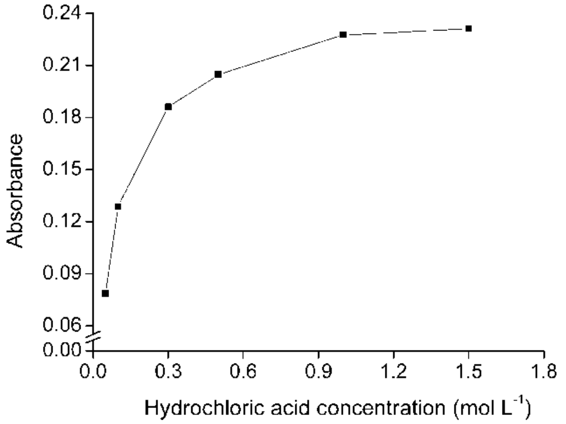

Figure 3. Effect of hydrochloric acid concentration on cadmium elution from a grape bagasse minicolumn.

100 μL of eluent. However, a decrease of only 16% was observed when the eluent volume was changed from 100 to 1000 μL. So, 100 μL was then chosen for further experiments.

Optimization of the elution conditions was performed in order to obtain the best results with a minimal concentration and volume of the eluent solution.

Effect of the Flow Rate of Preconcentration

Mass transfer from the solution to the binding sites of grape bagasse is affected by the preconcentration flow rate. This effect was investigated

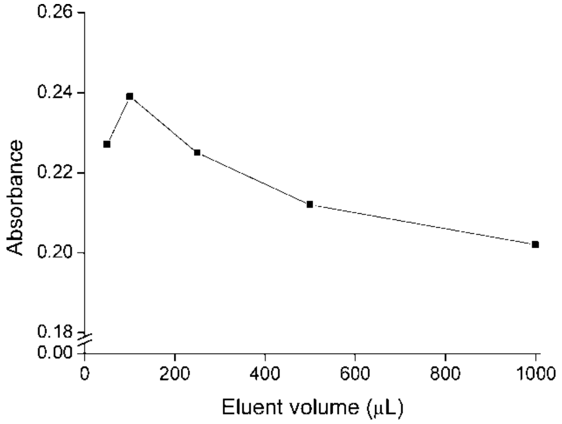

Figure 4. Influence of eluent volume (hydrochloric acid) on cadmium elution.

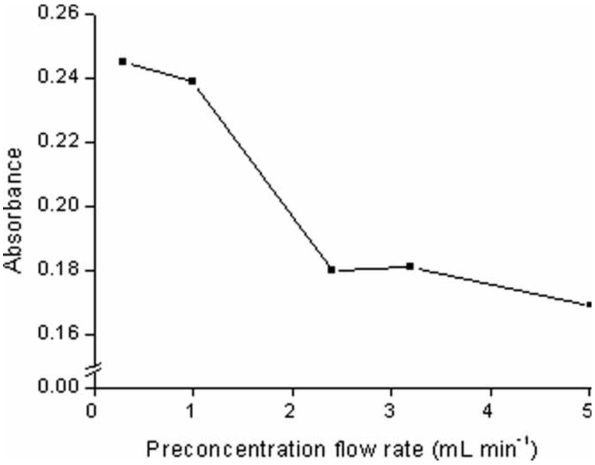

Figure 5. Influence of the flow rate of preconcentration on metal adsorption.

under the optimum conditions (pH, eluent type, concentration and eluent volume). The sample solution (4 mL) was passed through the minicolumn with the flow rate adjusted in the 0.3–5.0 mL min^{-1} range. A flow rate of 0.3 and 1.0 mL min^{-1} gives the best results for cadmium adsorption (Fig. 5). At flow rate higher than 2.0 mL min^{-1}, the metal ion adsorption was poorer, due to the kinetics involved in metal ion retention by the grape bagasse minicolumn. In addition, adsorption may decrease owing to the short contact time of analytes with the minicolumn at faster flow rates, resulting in incomplete adsorption. Therefore, 1.0 mL min^{-1} was chosen as preconcentration flow rate for subsequent experiments.

Concomitant Effect

Concomitant effects on the determination of 1.0 μg L^{-1} cadmium were evaluated. A given species was considered as concomitant if it resulted in an analytical signal variation of ±10% when compared with the analyte signal without concomitant.[22] These studies were carried out using binary solutions. The results obtained are shown in Table 1. The presence of Pb(II) ions in the proportion 1:1000 (Cd:Pb) decreased the Cd(II) analytical signal by ca. 12%. For other concomitants, only slight interferences were observed when an excess of the other ions (above 1:1000) was employed. As observed, the effects of some ions were negligible, and cadmium could be quantitatively determined in most samples without interference.

Table 1. Effect of the concomitant ions on Cd(II) adsorption using grape bagasse (n = 3)

Interferences	Ratio Cd(II) : concomitant	Recovery (%)
Co	1 : 1	105 ± 5
	1 : 100	96 ± 5
	1 : 1000	98 ± 4
Cu	1 : 1	104 ± 2
	1 : 100	100 ± 1
	1 : 1000	94 ± 3
Ni	1 : 1	101 ± 1
	1 : 100	99 ± 1
	1 : 1000	93 ± 0.4
Mn	1 : 1	103 ± 2
	1 : 100	98 ± 2
	1 : 1000	99 ± 3
Pb	1 : 1	102 ± 1
	1 : 100	97 ± 2
	1 : 1000	88 ± 1
Fe	1 : 1	101 ± 2
	1 : 100	99 ± 1
	1 : 1000	91 ± 0.4
Zn	1 : 1	101 ± 1
	1 : 100	97 ± 3
	1 : 1000	93 ± 2

Analytical Performance

The analytical features of the proposed method, such as precision, linear calibration range, limits of detection and quantification, were obtained. Precision, expressed as relative standard deviation (RSD), was estimated by applying successive preconcentration and elution cycles with 4 mL of cadmium solution (0.7 $\mu g\, L^{-1}$) under the optimum condition. These values are shown in Table 2.

The limits of detection and quantification were calculated according to the IUPAC recommendations. The enrichment factor (EF) was calculated as the ratio between the slopes of the analytical curves with and without the preconcentration step.[23] To calculate EF, a flow system of two channels coupled to the TS-FF-AAS system was used, one of them containing water as carrier and other using a sample loop of 100 μL. The same eluent volume was used in the preconcentration system. Others factors for characterizing online preconcentration systems, such as concentration efficiency (CE) and consumption index (CI), were also taken into account. CE is defined as the enrichment

Table 2. Analytical characteristics of the online cadmium preconcentration system using a grape bagasse minicolumn

Enrichment factor	33.7
Concentration efficiency (min^{-1})	8.425
Consumption index (mL)	0.119
Sample frequency (hr^{-1})	12
Precision (n = 18) (RSD, %)	4.6
Linear range ($\mu g\ L^{-1}$)	0.11–5.00
Regression equation ($\mu g\ L^{-1}$)	$-0.0016 + 0.1516\ C_{Cd}$
Analytical curve with the preconcentration step:	
Correlation coefficient	0.9983
Regression equation ($\mu g\ L^{-1}$)	$-0.0051 + 0.0045\ C_{Cd}$
Analytical curve without the preconcentration step:	
Correlation coefficient	0.9999
Limit of quantification ($\mu g\ L^{-1}$)	0.11
Limit of detection ($\mu g\ L^{-1}$)	0.03

factor achieved per minute, and CI is defined as the sample volume (mL) consumed for achieving an additional unit enrichment factor.[23] The sample volume and the preconcentration time used to calculate each were 4 mL and 4 min, respectively. Good limits of detection and higher enrichment factors could be reached by using higher preconcentration time.

In order to test the stability of grape bagasse, a 1.0 $\mu g\ L^{-1}$ cadmium solution was percolated through the minicolumn under the optimum conditions. In this way, the minicolumn was submitted to 80 successive preconcentration/elution cycles. The results indicate that the minicolumn allowed a large number of preconcentration/elution cycles with good precision (RSD 3.9%). Additionally, the Cd(II) recoveries were quantitative and good precision was attained with the proposed method. The repetitivity of the method was evaluated by sampling a 1.0 $\mu g\ L^{-1}$ cadmium solution in five different minicolumns. Each minicolumn was subjected to 10 preconcentration/elution cycles. The RSD value, considering all values from all minicolumns, was 5.0%.

Working with a 10-fold lower Cd concentration in the preconcentration system (1.0 $\mu g\ L^{-1}$), a 4 times higher signal was obtained relative to the system without preconcentration (Fig. 6).

Validation of the Method

In order to demonstrate the accuracy of the proposed enrichment and determination method, cadmium was determined in three certified reference

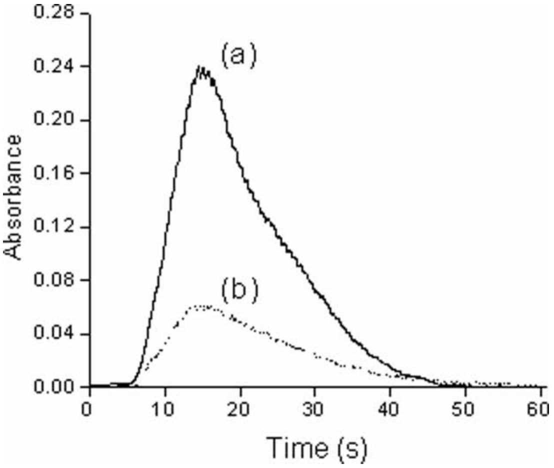

Figure 6. Signals obtained with and without preconcentration from TS-FF-AAS: (a) with preconcentration, 4 mL of 1 μg L^{-1} Cd(II) solution, using 100 μL of eluent; (b) without preconcentration, injected volume of 100 μL of 10 μg L^{-1} Cd(II) solution.

Table 3. Results for cadmium determination in certified reference materials obtained by the proposed system (n = 3)

Sample	Certified value (μg/g)	Found value (μg/g)	Recovery (%)
BCR-189	0.0713 ± 0.003	0.0781 ± 0.004	109.6 ± 4.9
BCR-191	0.0284 ± 0.0014	0.0269 ± 0.003	94.9 ± 9.8
BCR-281	0.120 ± 0.003	0.1119 ± 0.004	93.3 ± 3.0

materials. The results are summarized in Table 3. As can be seen, good accuracy of the method was obtained because of good agreement with the certified value (RSD less than 10%).

CONCLUSIONS

The proposed online preconcentration system coupled to the TS-FF-AAS technique allows attaining good analytical characteristics, as well as presenting a simple flow design, thus extending the TS-FF-AAS applicability. The characteristics can be checked by comparing some information from the proposed method to those recently proposed for cadmium preconcentration (Table 4). When necessary, the system also permits employing higher preconcentration times (>4 min), which can increase the detectivity of the method. Additionally, a by-product (grape bagasse) was successfully applied for preconcentration

Table 4. Comparative data from some recent proposals for cadmium preconcentration

Adsorbent material	LOD (μg L^{-1})	LOQ (μg L^{-1})	Enrichment factor	References
Grape bagasse	0.03	0.11	33.7	This work
Knotted reactor	0.10	0.33	18	[24]
Chelating polymer	15	—	—	[25]
Chromosorb-106 resin	0.19	—	250	[26]
Poly-Cd(II)-DAAB-VP resin	0.09	0.21	200	[27]

LOD = limit of detection; LOQ = limit of quantification.

purposes with good selectivity and accuracy. This last characteristic was checked using certified reference materials, and no differences in the results at the 95% confidence level were observed.

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