

*Original Paper*

## Online preconcentration system for determining ultratrace amounts of Cd in vegetal samples using thermospray flame furnace atomic absorption spectrometry

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**Abstract.** A system has been developed for online preconcentration and determination of Cd using thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). It is based on the solid-phase extraction of Cd in an Amberlite XAD-2 minicolumn loaded with 2-(2-thiazolylazo)-5-dimethylamino-phenol (TAM), and the metal ion is eluted with 1 mol L<sup>-1</sup> hydrochloridric acid, followed by its determination. The online system allows determining Cd with a detection limit of 8.0 ng L<sup>-1</sup> and a quantification limit of 25.0 ng L<sup>-1</sup>. The precision (repeatability), calculated as the relative standard deviation (% RSD) in sample solutions containing 0.5 and 3.0 µg L<sup>-1</sup> of Cd, was 6.1 and 4.5%, respectively. The preconcentration factor obtained was 24. The system's accuracy was confirmed by analyzing the following certified reference materials (CRMs): Rice flour NIES 10b, Apple leaves NIST 1515 and Orchard leaves NBS 1571. This procedure was applied to the determination of Cd in cabbage and powdered guarana samples.

**Key words:** TS-FF-AAS; Cd determination; vegetal samples.

Cadmium is a natural constituent element of the earth's crust. However, its concentration in a given environment may increase in response to anthropogenic sources of contamination. The presence of this metal in the environment may result from its widespread use (fertilizers, mining, pigments), from burning oil and coal, and from the incineration of waste, causing extensive contamination of the soil, air, and water. Cadmium is characterized by its prolonged persistence in the environment and in living organisms, which accounts for its bioaccumulation. This element is absorbed by plants and then transferred to animals through the food chain. Thus, the metabolism and toxicology of cadmium are of major concern, since it has a high toxic potential [1, 2].

Procedures for determining trace amounts of Cd are important because contamination levels must be monitored constantly, especially in biological, food and environmental samples. However, since a variety of matrices show very low concentrations of Cd, preconcentration procedures are often required to allow its quantification. Therefore, many enrichment procedures for determining Cd have been developed, involving different methods, e.g., liquid–liquid extraction [3], coprecipitation [4], cloud point extraction [5] and solid phase extraction [6–9].

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**Table 1.** Characteristics of some online preconcentration systems developed for determining metals using TS-FF-AAS

Metal	Sample	Solid phase	Complexing reagent	LOD ( $\mu\text{g L}^{-1}$ )	Reference
Cd	Vegetal samples	Amberlite XAD-2	TAM	0.080	this study
Cd	Waters	PUF	DDTP	0.22	[34]
Pb	Vegetal samples	PUF	DDTP	1.5	[35]
Cd	Waters	C <sub>18</sub>	APDC	0.007	[36]
Pb				0.17	
Cd	Water and biological materials	PUF	DDTP	0.12	[37]
Cd	Mineral and tap waters	Mixture of C <sub>60</sub> and C <sub>70</sub>	APDC	0.1	[38]
Pb				2.4	

*SPE* Solid phase extraction; *CPE* cloud point extraction; *PUF* polyurethane foam; *LOD* limit of detection; *TAM* 2-(2-thiazolylazo)-5-dimethylaminophenol, *DDTP* ammonium 0,0-diethyldithiophosphate; *APDC* ammonium pyrrolidinedithiocarbamate.

Analytical procedures involving solid phase extraction [10] have become common due to their many advantages, including the availability and easy recovery of the solid phase, achievement of high preconcentration factors and efficiency. At this point, some researchers applied online preconcentration using solid-phase extraction to develop procedures with analytical characteristics suitable for determining metal ions in a variety of samples using different spectroanalytical techniques [11], such as FAAS [12–14], GF AAS [15–17], ICP OES [18–20] and ICP-MS [21].

Although FAAS is a consolidated technique, there is a great demand for improving its sensitivity, particularly to elements with a high detection limit or elements that are present in very low concentrations in samples [22]. A recent alternative to improve the sensitivity of this technique is the coupling of thermospray generation in a flame furnace to atomic absorption spectrometry (TS-FF-AAS) to determine more volatile elements such as Cd.

In TS-FF-AAS, a nickel tube is placed on a standard burner head from a flame AAS instrument connected with a ceramic capillary, which presents an end inside the flame-heated tube. Thus, the thermospray is generated inside the nickel furnace when the sample flows through the capillary heated zone. This technique can lower the detection limit of volatile metallic species considerably in comparison with FAAS, principally due to some of its characteristics, such as high efficiency in the transportation of samples to the atomizer and the confinement of atoms inside the flame furnace. Hence, these characteristics enhance the sensitivity of AAS when this trap manifold is used [23, 24]. Several reports describe the application of this technique to the direct determination of metal in different matrices [25–31].

Recently, preconcentration procedures based on online solid phase extraction have been coupled to the TS-FF-AAS technique to improve its sensitivity (Table 1). When TS-FF-AAS is coupled with a preconcentration procedure such as solid-phase extraction, it can reach very low detection limits comparable to those obtained with graphite furnace absorption spectrometry (GF AAS), thus justifying the use of these two analytical tools.

This paper proposes an online preconcentration system for determining Cd in vegetal samples using thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). The procedure is based on the solid-phase extraction of Cd in the form of 2-(2-thiazolylazo)-5-dimethylaminophenol (TAM) complexes on Amberlite XAD-2 and the elution of these ions using hydrochloridric acid, followed by its determination by TS-FF-AAS.

## Experimental

### Instrumentation

A Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis. The Cd hollow cathode lamp was operated according to the manufacturer's recommendations (Table 2).

Two Alitea C-6 XV (Stockholm, Sweden) peristaltic pumps equipped with Tygon tubes were used to propel all the solutions. A Rheodine model 5041 (Cotati, California, USA) four-way manual valve was used to select the preconcentration/elution steps. All the

**Table 2.** Operating parameters of the flame atomic absorption spectrometer for cadmium determination using TS-FF-AAS

Wavelength	228.8
Lamp current (mA)	4.0
Slit width (nm)	0.5
Burner height (mm)	10.0
Acetylene flow rate ( $\text{mL min}^{-1}$ )	2.00
Air flow rate ( $\text{mL min}^{-1}$ )	13.50

connections, i.e., fittings and two- and three-way joints, were made of plastic and PEEK materials. The manifold was made of a PTFE tube with an 0.5 mm i.d.

The TS-FF-AAS system consisted of a thermospray flame furnace unit built in-house, which included a ceramic capillary (0.5 mm i.d., 2.0 mm e.d., and 100 mm length) and a Ni tube (10 cm) attached to the burner by an in-house built stainless steel support fixed with four ceramic pins. The tube was laid upon these pins and could be moved into and out of the flame. To raise the temperature inside the tube, six 2 mm diameter holes were drilled into the bottom of the tube. Another hole was drilled at a 90° angle from the bottom holes to insert the thermospray capillary. The capillary tip was inserted about 1 mm into the tube furnace. The manifold was assembled with 0.5 mm i.d. PTFE tubing [32].

#### Reagents and solutions

All the reagents were of analytical grade unless otherwise stated. All the solutions were prepared with ultrapure water supplied by an EASYpure RF water purification system (18.3 MΩ cm, Barnstedt, Dubuque, IA, USA). Nitric acid and ethanol were of Suprapure quality (Merck). Laboratory glassware was kept overnight in a 10% nitric acid solution. Before use, the glassware was rinsed with deionised water and dried in a dust-free environment.

Cadmium solutions (Merck) were prepared by diluting 1000 μg mL<sup>-1</sup> standard solutions (in 1% hydrochloric acid solution) to the desired concentrations.

TAM 0.05% (Aldrich) was prepared by dissolving 0.10 g of 2-(2-thiazolylazo)-5-dimethylaminophenol in 200 mL ethanol (Merck).

#### Minicolumn preparation and evaluation of its phase transfer factor

TAM solution (0.05%, w/v) was percolated through a 4.50 cm long laboratory-made cylindrical minicolumn with an internal diameter of 4.0 mm, containing about 0.10 g of Amberlite XAD-2, at a flow rate of 5.0 mL min<sup>-1</sup> for 15 min. The column was then washed with a 10% (w/v) sodium hydroxide solution until the purple effluent became colourless, to remove excess TAM, after which it was washed with 5% (v/v) hydrochloric acid solution and deionised

water at the same flow rate. Washing with nitric acid was necessary to prevent possible metal contamination.

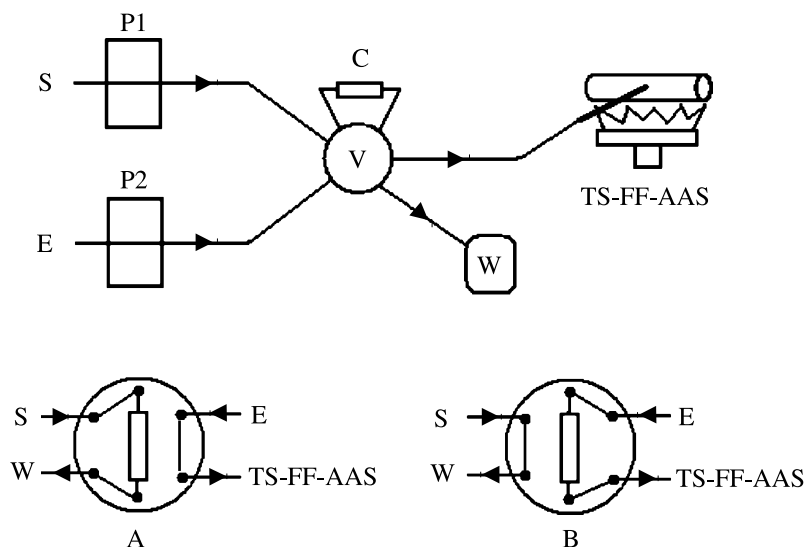
To evaluate the phase transfer factor of the minicolumn, 5 mL of a cadmium solution (5.0 μg L<sup>-1</sup>) was percolated through the column under the optimum conditions found for the preconcentration system. Subsequently, 2 mL of HCl solution (1 mol L<sup>-1</sup>) was used to elute the adsorbed cadmium. Then the cadmium concentration was determined after extraction using TS-FF-AAS, and its recovery was calculated according to Fang [33].

#### Sample preparation

The following certified reference materials (CRMs) were analyzed: Rice flour NIES 10b, Apple leaves NIST 1515 and Orchard leaves NBS 1571. Non-certified cabbage and powdered guarana samples also were analysed. To decompose the samples, 0.25–0.5 g of material was treated with 4.0 mL of HNO<sub>3</sub> 1:1 (v/v) and steeped overnight in a Teflon vessel, after which the vessel was closed and placed in a pressurized digestion system, which was heated on a stove at 120 °C for 16 h. After cooling to room temperature, these solutions were adjusted to pH 8.0 with a 10% (w/v) sodium hydroxide solution and a borate buffer solution, completing the volume to 50 or 25 mL.

#### Online preconcentration system for Cd determination

A diagram of the online preconcentration system is shown in Fig. 1. The flow system was built using two peristaltic pumps fitted with Tygon tubes, a four-way valve and a minicolumn packed with Amberlite XAD-2 resin loaded with TAM, coupled to the thermospray flame furnace atomic absorption spectrometer (TS-FF-AAS). The flow system was operated in time-based mode. A sample solution (S) containing 0.5–5.0 μg L<sup>-1</sup> of Cd was buffered at pH 8.0 with a borate buffer solution and pumped at 5.0 mL min<sup>-1</sup>, percolating through a minicolumn that retained the Cd ions by chemisorption, complexed with TAM. The remaining solution was discarded (W). When the injection valve was switched on, the Cd was displaced by a 1.0 mol L<sup>-1</sup> stream of hydrochloric acid (E) flowing at 2.0 mL min<sup>-1</sup>. The eluate was placed directly into the thermospray flame furnace system. Signals were recorded as peak area, using the instrument's software. The minicolumn did not require



**Fig. 1.** Schematic diagram of the flow system used for the preconcentration and determination of Cd by TS-FF-AAS. *S* Sample, *E* eluant (HCl 1 mol L<sup>-1</sup>), *P1* peristaltic pump 1 (5.0 mL min<sup>-1</sup>); *P2* peristaltic pump 2 (2.0 mL min<sup>-1</sup>); *(C)* Amberlite XAD-2/TAM minicolumn; *V* four-way valve; *TS-FF-AAS* thermospray flame furnace atomic absorption spectrometer and *W* waste. *(A)* Four-way valve in the preconcentration step, and *(B)* four-way valve in the elution position

reconditioning at the end of each cycle because the samples were buffered before the preconcentration step. The sampling rate achieved was 60 samples per hour for a preconcentration time of 30 s (sample consumption of 2.5 mL) and an elution time of 30 s.

## Results and discussion

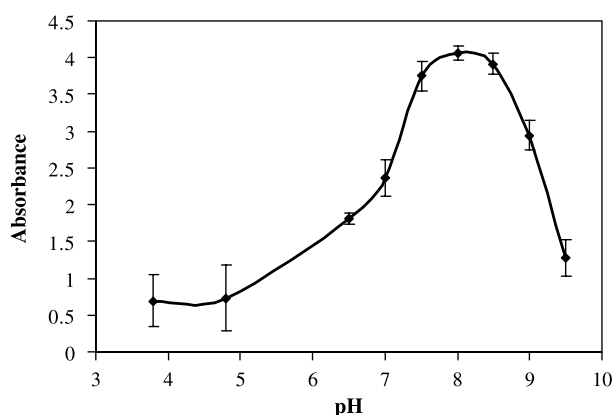
To determine the optimal conditions for maximum extraction of Cd on an Amberlite XAD-2/TAM minicolumn and its determination by TS-FF-AAS, several parameters were assessed using a standard solution containing a  $5.0 \mu\text{g L}^{-1}$  concentration of metal. The eluant flow rate was set at  $2.0 \text{ mL min}^{-1}$ , which is the condition required for the formation of thermospray.

### Effect of pH

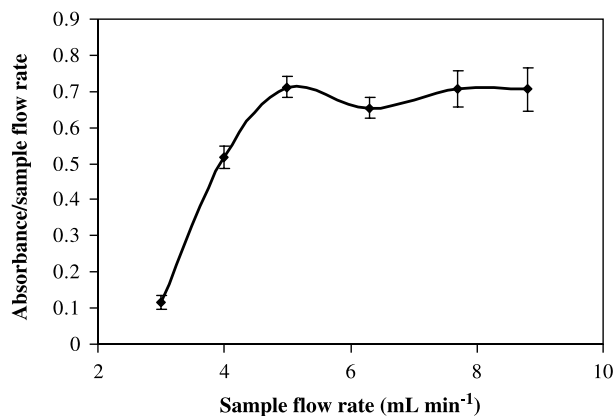
The effect of pH on the sorption of Cd on resin inside the minicolumn was studied within a pH range of 3.8–9.5, as indicated in Fig. 2. The pH was controlled with acetate buffer for pH 3.8 and 4.8, phosphate buffer for pH 6.5 and 7.0, and borate buffer for pH 8.0 and 9.0 (all in a final concentration of  $0.002 \text{ mol L}^{-1}$ ). The borate buffer pH 8.0 was suggested since this solution provides a higher analytical signal. A decrease in signal after this pH value can possibly be explained by the adsorption of hydroxides at the tubing walls.

### Effect of sampling flow rate

The effect of the sample flow rate on Cd extraction through the minicolumn was studied by varying the flow rate from  $3.0$  to  $8.8 \text{ mL min}^{-1}$  at the optimal pH established in the previous experiment. The results



**Fig. 2.** Effect of pH on the retention of Cd in the column. Conditions: sample flow rate  $6.0 \text{ mL min}^{-1}$ , buffer concentration  $0.002 \text{ mol L}^{-1}$ , eluant flow rate  $2.0 \text{ mL min}^{-1}$ , and HCl concentration  $0.5 \text{ mol L}^{-1}$



**Fig. 3.** Effect of sample flow rate on the retention of Cd in the column. Conditions: pH 8.0, buffer concentration  $0.002 \text{ mol L}^{-1}$ , eluant flow rate  $2.0 \text{ mL min}^{-1}$ , and HCl concentration  $0.5 \text{ mol L}^{-1}$

in Fig. 3 indicate that the efficiency of Cd retention on the resin reached its maximum at a flow rate of  $5.0 \text{ mL min}^{-1}$ . The values of the analytical signal increased along with the samples' flow rate, but the retention efficiency calculated by dividing the signal by the sample's flow rate remained constant above this value.

### Effect of the eluant concentration

The effect of the eluant concentration, which was a hydrochloric acid solution, was also investigated. In this system, where the minicolumn is not reconditioned, this is a very important factor because the HCl solution must provide fast elution of Cd from the loaded resin in order to produce a well-defined and reproducible peak.

On the other hand, a highly acidic eluant reduces the ability of the column to recover the pH in the sampling step. This high acidity diminishes ion sorption on the resin, reducing the extraction efficiency. Thus, the acid concentration was studied in four concentrations ( $0.1$ ,  $0.5$ ,  $1.0$  and  $2.0 \text{ mol L}^{-1}$ ). Decreasing signal values with decreasing concentrations of HCl were observed, which is explained by a possible incomplete desorption of cadmium from the minicolumn. The optimum eluant concentration achieved was a solution of  $1 \text{ mol L}^{-1}$  HCl.

Nitric acid was also tested in the elution of cadmium from the minicolumn. The same hydrochloric acid concentrations produced similar signals. On the other hand, the time of utilization of the minicolumn decreases when using nitric acid. Thus, hydrochloric acid was chosen as the better eluant for this application.

### Effect of final buffer concentration

The final concentration of borate buffer (pH 8.0) in the sample solutions was studied. An adequate buffer concentration is important to ensure the rapid recovery of the pH in the column and allow for maximum efficiency in the extraction of Cd. The buffer concentration influence was studied from 0.001 to 0.004 mol L<sup>-1</sup>. The analytical signal reached its highest values at a buffer concentration of 0.002 mol L<sup>-1</sup>.

### Effect of other ions

To evaluate the effects of other metal ions on the preconcentration procedure, a sample solution containing a concentration of 5.0 µg L<sup>-1</sup> of Cd was prepared and analysed by the proposed method. The results showed that a concentration of 50.0 µg L<sup>-1</sup> of Cu<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>6+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Mo<sup>4+</sup>, Sb<sup>5+</sup> and V<sup>5+</sup> does not interfere with the determination of Cd by the proposed procedure.

### Analytical characteristics

The calibration method used here was based on the preparation of analytical curves from standard solutions, which were also applied to the preconcentration procedure. The system showed linearity within the concentration range of 0.025–5.0 µg L<sup>-1</sup> for a 30 s preconcentration time. The calibration graphs, under the optimum chemical and flow conditions using the manifold depicted in Fig. 1 showed Abs = 0.7902 [Cd, µg L<sup>-1</sup>] – 0.1411 in the interval of 0.025–5.0 µg L<sup>-1</sup> ( $R = 0.9983$ ). By direct TS-FF-AAS determination, without the preconcentration system and also using the peak area as analytical signal, the linear range was between 5 and 50 µg L<sup>-1</sup>. The calibration equation was Abs = 0.0326 [Cd, µg L<sup>-1</sup>] – 0.0719 ( $R = 0.9991$ ). The experimental preconcentration factor, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, was 24.2.

Under these conditions, the phase transfer factor (defined as the ratio between the analyte mass in the original sample and that in the concentrate) was 60.5%. The concentration efficiency (defined as the product of the enrichment factor and the sampling frequency per number of samples analyzed per minute) was also calculated and also found to be 24.2 min<sup>-1</sup>. The analytical frequency was 60 samples h<sup>-1</sup>. The consumption index is a parameter that provides information

**Table 3.** Results obtained for the determination of Cd (µg g<sup>-1</sup>) in the CRMs and the cabbage sample analyzed ( $n = 3$ )

Sample	Proposed methodology	Certified value
Rice flour NIES 10b	0.33 ± 0.02	0.32 ± 0.02
Orchard leaves NBS 1571	0.10 ± 0.01	0.11 ± 0.01
Apple leaves NIST 1515	0.015 ± 0.002	0.013 ± 0.002
Cabbage	0.11 ± 0.02	–
Powdered guarana	1.27 ± 0.05	–

about the amount of sample volume necessary to achieve a unit of enrichment factor. The consumption index found for this preconcentration system was 0.10 mL [33].

The detection and quantification limits, defined as LOD = 3δ/S and LOQ = 10δ/S, where S is the slope of the analytical curve, and δ is the standard deviation of ten consecutive measurements of the blank signal, were also calculated. The LOD found was 8.0 ng L<sup>-1</sup>, and the LOQ was 25.0 ng L<sup>-1</sup>.

The precision of the procedure, determined as the relative standard deviation (RSD,  $n = 10$ ) in sample solutions containing 0.5 and 3.0 µg L<sup>-1</sup> of Cd, was 6.1 and 4.5%, respectively.

### Accuracy of the method and application

To evaluate the accuracy of the new procedure, Cd was determined in three reference materials, two supplied by the National Institute of Standards and Technology (Gaithersburg, MD, USA): Apple leaves NIST 1515 and Orchard leaves NBS 1571 and another reference material provided by the National Institute for Environmental Studies (NIES, Japan): Rice flour NIES 10b. The procedure was also applied to determine the concentration of Cd in a sample of cabbage. The results in Table 3 show that the new procedure can be applied to determine Cd in vegetal samples.

### Conclusions

The online preconcentration system proposed here is simple, efficient and can be applied to the determination of Cd in vegetal samples. When coupling the step of preconcentration by solid phase extraction before the determination of Cd by thermospray flame furnace atomic absorption spectrometry, it is possible to determine the presence of very low concentrations of this metal in vegetal matrices (in the order of ng g<sup>-1</sup>). The proposed procedure presents detection limits

comparable to those achieved by graphite furnace atomic absorption spectrometry for this element.

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