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Analytical note

Application of polyurethane foam loaded with BTAC in an on-line preconcentration system: cadmium determination by FAAS

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Abstract

In the present paper, the use of polyurethane foam modified by 2-(2-benzothiazolylazo)-2-*p*-cresol (BTAC) as a sorbent in an on-line preconcentration system to determine cadmium trace levels by FAAS is proposed. The procedure was based on the chemical sorption of cadmium (II) ions onto a minicolumn packed with polyurethane foam, followed by 0.10 mol l⁻¹ hydrochloric acid elution and direct determination by Flame Atomic Absorption Spectrometry. The flow system was operated in a time-based mode. Chemical and flow variables were studied. Results demonstrated that sample solutions containing cadmium(II) in the range of concentration from 0.91 to 30.00 μg l⁻¹, pH between 6.50 and 9.25 could be determined by this procedure, in a preconcentration time of 1 min. Flow rates in preconcentration and elution steps were 7.00 and 4.00 ml min⁻¹, respectively. The precision of the preconcentration procedure (evaluated as standard deviation of solutions containing 1.0–30.0 μg l⁻¹ of cadmium) varied in the range from 5 to 1%. The preconcentration factor, calculated as the ratio of the linear section of the slopes of the analytical curves before and after preconcentration, was 41, for a volume sample of 7.00 ml. The detection limit was 0.27 μg l⁻¹ for a preconcentration time of 1 min. The proposed procedure was applied for

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determination of cadmium in biological reference materials. Achieved results demonstrated that the procedure can be applied for analysis of biological materials with satisfactory accuracy. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Flame Atomic Absorption Spectrophotometry (FAAS) [1] is an analytical technique remarkable for its selectivity, speed and fairly low operational cost. However, sometimes this technique does not have enough sensitivity for the required analysis. Then procedures for an on-line preconcentration [2] have been proposed to widen FAAS application.

The process of solid phase extraction [3] has been accepted due to many possible advantages including availability and easy recovery of the solid phase, achievement of high preconcentration factors and ease of separation and enrichment using continuous flow systems. Furthermore, they usually do not need organic solvents which may be toxic.

Among many available materials for solid phase extraction, polyurethane foam was proposed as a sorbent by Bowen [4] in 1970 and since then it has been used in many processes operating by batch and off-line column. Polyurethane foam was used by many authors in cadmium extraction processes. Lypka et al. [5] proposed the use of benzoylacetone-treated polyurethane foam for extraction and separation of cadmium and copper. Hamza et al. [6] used modified polyurethane foam modified by dithizone for the detection and semiquantitative determination of cadmium. Hu et al. [7] used open cell polyurethane foam loaded with 8-hydroxyquinoline-phenolphthalein for preconcentration of trace cadmium in water. Chakrabarti and Roy [8] proposed a spectrophotometric method for cadmium determination after selective extraction of cadmium(II)-phenantroline complex onto polyurethane foam.

Use of polyurethane foam as sorbent in an on-line enrichment system was recently proposed by Jesus et al. [9]. In it, a minicolumn containing unloaded polyurethane foam was employed to

preconcentrate zinc [8,10]. The same authors also developed on-line separation systems for the determination of nickel [11] and aluminum [12].

In the present paper, the use of modified polyurethane foam by 2-(2-benzothiazolylazo)-2-*p*-cresol (BTAC) reagent as a sorbent in an on-line preconcentration system to determine cadmium trace levels by FAAS is proposed. 2-(2-Benzothiazolylazo)-2-*p*-cresol (BTAC) reagent was first synthesized by Gusev et al. [13] and has been used in spectrophotometric determinations of thallium [14]. The formed complex in the reaction between cadmium(II) and BTAC shows a maximum absorption at 610 nm and molar absorptivity of $4.5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ [15].

2. Experimental

2.1. Apparatus

A Varian (Mulgrave, Victoria, Australia) Model SpectrAA 220 flame atomic absorption spectrometer was used for the analysis. The cadmium hollow cathode lamp was run under the conditions suggested by the manufacturer (current: 4.0 mA). The wavelength (228.8 nm), the bandwidth of the slit (0.5 nm) and burner height (13.5 mm) had suggested values. The flame composition was: acetylene (flow rate: 2.0 l min^{-1}) and air (flow rate: 13.5 l min^{-1}). Aspiration flow rate was 4.0 ml min^{-1} .

An Alitea USA peristaltic pump C-6 XV (Stockholm, Sweden) furnished with Tygon tubes was used to propel all solutions and a Rheodyne 5041 (CA, USA) model injection valve was used to select the preconcentration/elution steps. All connections were made using fittings, unions and tees made of plastic and PEEK materials. The

manifold was built up with PTFE tube of 0.5 mm bore.

A Digimed DM 20 (Santo Amaro, Brazil) pH meter was also used.

2.2. Reagents

Ultrapure water from a Milli-Q (Barnstead, Dubuque, USA) water purification system (Millipore) was used to prepare all solutions.

All reagents were of analytical grade. The hydrochloric acid was suprapur quality (Merck, Darmstadt, Germany). The laboratory glassware was kept overnight in a 5% nitric acid solution. Afterwards it was rinsed with deionized water and dried in a dust-free environment.

Cadmium(II) solution ($1.00 \mu\text{g ml}^{-1}$) was prepared by diluting a $1000 \mu\text{g ml}^{-1}$ cadmium solution (atomic absorption Aldrich) with a 5% hydrochloric acid solution.

BTAC solution (0.04% w/v) was prepared by dissolving 0.040 g BTAC in 100 ml of absolute ethanol (Merck).

Ammonium buffer solution (pH 9.00) was prepared by dissolving 53.50 g of ammonium chloride (Merck) in 1000 ml of deionized water and adjusting pH with ammonium hydroxide.

Hydrochloric acid (0.1 mol l^{-1}) was prepared by direct dilution with deionized water from the concentrated suprapur solution.

Polyurethane foam commercial, open-cell, polyether-type PUF (Atol) was pulverized and used as previously described by Ferreira et al. [16].

2.2.1. Preparation of the solid sorbent

BTAC solution 0.040% (w/v) was percolated through a minicolumn containing approximately 0.1 g of polyurethane foam at a flow rate of 2.5 ml min^{-1} for 5 min. Afterwards, the column was washed with 25% v/v ammonium hydroxide solution until the liquid eluted from the column become clear. Then, the column was washed with deionized water at the same flow rate.

2.3. Reference materials and its decomposition

For accuracy studies several certified reference materials supplied by the National Institute for

Environmental Studies (NIES), Japan, NIES 10b — rice flour unpolished, medium level of cadmium and NIES 10c — rice flour unpolished, high level of cadmium; the National Research Council, Canada, TORT-1-lobster hepatopancreas and the National Institute of Standard and Technology NIST, USA, NIST 1577b — bovine liver were analyzed. To decompose these materials, a convenient amount of each sample was weighed and treated with nitric acid 1:1 (v/v) overnight in a Teflon vessel. Afterwards the Teflon vessel was closed and put into a stove at 170°C for 16 h. After cooling at room temperature these solutions were adjusted to pH 9.00 with ammonium hydroxide and made up to the required volume.

2.4. Continuous flow system

A diagram of the flow system is shown in Fig. 1. The flow system was made up of a peristaltic pump fitted with Tygon tubes, one four-way valve and a minicolumn packed with polyurethane foam loaded with BTAC, and it was coupled to a flame atomic absorption spectrometer. The flow system was operated in a time-based mode, in which a sample solution (S) pumped at 7.00 ml min^{-1} percolated through a minicolumn that held the solid sorbent. Then, cadmium(II) ions are retained by chemical sorption as cadmium(II)-BTAC complex and the remaining solution was discharged. By switching the injection valve a stream of 0.1 mol l^{-1} hydrochloric acid (E) that flows at 4.00 ml min^{-1} displaces the cadmium complex. This eluate was taken direct to the nebulizer-burner system of the flame atomic absorption spectrometer. Preconcentration time was 1 min. Signals were measured as peak height by using an instrument software. It was not necessary to recondition the minicolumn at the end of each cycle since samples were buffered by ammonium buffer solution before preconcentration. However, if hydrochloric acid concentration was higher than 0.25 mol l^{-1} , the column should be washed with ammonium buffer solution for 10 s after each elution. The number of preconcentrations without reconditioning performed using a only column is higher than 300. Achieved sam-

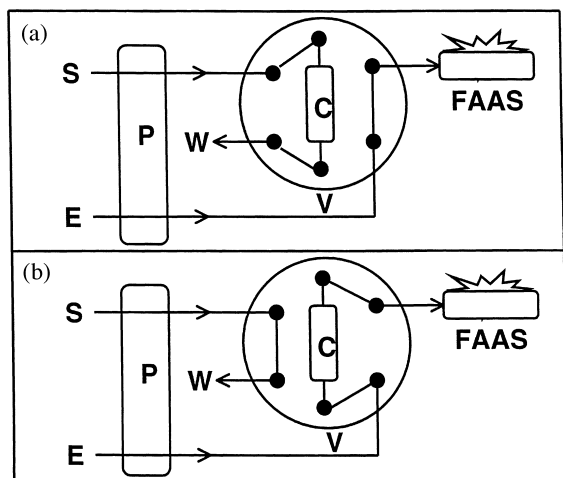


Fig. 1. Schematic diagram of the flow system used for preconcentration and determination of cadmium by FAAS: S, sample (7.00 ml min^{-1}); E, eluent (4.00 ml min^{-1}); P, peristaltic pump; C, polyurethane foam/BTAC minicolumn; V, four-way valve; FAAS, flame atomic absorption spectrometer and W, waste. A, four-way valve in the preconcentration step and B, four-way valve in the elution position.

pling rate was 48 samples per hour. Calibration solutions were submitted to the same preconcentration procedure.

3. Results and discussion

3.1. Flow system performance

The continuous flow system was optimized by using the univariate method in order to determine the best chemical and flow conditions for cadmium determination with a good sensitivity.

Chemical variables were studied firstly. A standard solution containing $10.00 \mu\text{g l}^{-1}$ of cadmium was continuously injected into the flow system shown in Fig. 1. A time-based technique equivalent to use 7.0 ml of sample (sample flow rate 7.0 ml min^{-1} ; in a pumping time of 60 s) was chosen. The effect of the sample pH on the cadmium response was investigated within the range from 3.0 to 10.0 . Maximum retention occurred within the pH range of 6.50 to 9.25 . Therefore, pH 9.00 was selected for subsequent work, as at this pH the ammonium buffer shows a good buffer index.

The elution of cadmium from the minicolumn was studied using hydrochloric acid solutions as stripping agent at different concentrations (0.01 – 3.0 mol l^{-1}). Total elution was reached in concentrations over 0.05 mol l^{-1} . Accordingly, 0.1 mol l^{-1} hydrochloric acid was selected for use as eluent in further studies.

The effect of the sample flow rate in the proposed system was also studied. Three milliliters of a solution containing $10 \mu\text{g l}^{-1}$ of cadmium was injected into the system at flow rates from 1.6 to 16.7 ml min^{-1} . Results shows that the analytical signals decreased slowly on increasing flow rates. It indicated that the cadmium sorption kinetics is fast. This way, a flow rate of 7.00 ml min^{-1} was chosen, because larger flow rates allows using high sample volumes, which can improve the preconcentration factor.

The performance of the flow system with PUF-BTAC as solid sorbent was also assessed by using $10 \mu\text{g l}^{-1}$ cadmium solution, sample flow rate of 7.00 ml min^{-1} , and preconcentration times that varied from 1.0 to 6.0 min . The FAAS analytical signal increased proportionally on increasing preconcentration time, which means that the retention efficiency was constant for this time interval. In these conditions the retention efficiency [2,2], also referred to as the phase transfer factor, defined as the ratio between the analyte mass in original sample and that in the concentrate, was 0.73 .

The influence of the 0.1 mol l^{-1} hydrochloric acid solution flow rate during the cadmium desorption step from the minicolumn was also investigated. Results demonstrated that the analytical signal is maximum and constant at a flow rate in the range of 3.4 – 4.6 ml min^{-1} . Thus, a flow rate of 4.00 ml min^{-1} was selected in further studies. Flow rates lower than 3.4 ml min^{-1} decreased the analytical signal considerably, possibly due to the low desorption kinetics.

3.2. Selectivity of the proposed procedure

In order to determine the selectivity of the method, solutions containing cadmium and other ions were prepared and analyzed by the proposed procedure. Studies made using $10.0 \mu\text{g l}^{-1}$ of

Table 1
Effect of ions in determination of cadmium in continuous flow system

Interferent	Ratio Cd(II)/ion
Al ⁺³	1:500
Ba ⁺²	1:1000
Br ⁻	1:1000
Ca ⁺²	1:10 000
Cl ⁻	1:150 000
Cr ⁺³	1:1000
Cu ⁺²	1:200
F ⁻	1:1000
Fe ⁺³	1:1000
K ⁺	1:20 000
Mg ⁺²	1:100
Mo ⁺⁵	1:1000
Na ⁺	1:150 000
NO ₃ ⁻	1:20 000
Pb ⁺²	1:50
S ₂ O ₃ ⁻	1:1000
SO ₄ ⁻²	1:1000
Zn ⁺²	1:200

cadmium(II) solution, represented in Table 1, do not show any interference in cadmium determination by FAAS after the on line preconcentration procedure developed in this work.

3.3. Analytical features

The flow system for 1 min preconcentration time shows linearity in the concentration range from 0.91 to 30.00 $\mu\text{g l}^{-1}$. The calibration curves under the optimum chemical and flow conditions, made up by using the manifold depicted in Fig. 1, was calculated as $A = 0.00822 + 0.00989$ ($\text{Cd } \mu\text{g l}^{-1}$) in the range of 0.0–30 $\mu\text{g l}^{-1}$. By using direct aspiration, without preconcentration, the linear range took place between 10.0 and 400.0 $\mu\text{g l}^{-1}$ [$A = -0.000248 + 0.000241$ ($\text{Cd } \mu\text{g l}^{-1}$)]. The experimental preconcentration factor [2,17], calculated as the ratio of the slopes of the calibration curves obtained with and without preconcentration, was 41, for the 1-min preconcentration time. Sample volumes greater than 7.00 ml (> 1 min preconcentration time) can be used and, thus, higher preconcentration factors can be achieved.

The precision of the continuous preconcentration method, evaluated as the relative standard deviation for sample solutions containing 0.91–30.00 $\mu\text{g l}^{-1}$ of cadmium, varied from 5 to 1%, respectively, both by making seven measurements of each solution.

The limit of detection (LOD), defined as the concentration of cadmium that gives an equivalent response to three times the standard deviation (S.D.) of the blank ($n = 11$), was found to be 0.27 $\mu\text{g l}^{-1}$ also by using 7.00 ml of the sample solution. The limit of quantification (LQ) was found to be 0.91 $\mu\text{g l}^{-1}$.

3.4. Determination of cadmium in certified reference materials

The accuracy of the proposed procedure was evaluated by analysis of several certified reference materials. Results can be seen in Table 2.

The *t*-test paired was applied for achieved results. It was found that there is no significant difference between achieved results by the proposed procedure and certified values.

Table 2
Results obtained for analyzed certified reference materials ($n = 3$)^a

Sample	Cadmium found by proposed methodology ^b ($\mu\text{g g}^{-1}$)	Certified values ($\mu\text{g g}^{-1}$)
Rice flour NIES 10b	0.31 \pm 0.02	0.32 \pm 0.02
Rice flour NIES 10c	1.85 \pm 0.03	1.82 \pm 0.06
Bovine liver NIST 1577b	0.48 \pm 0.02	0.50 \pm 0.03
Lobster hepatopancreas tort-1 NRCC	25.45 \pm 0.70	26.30 \pm 2.10

^aAbbreviations: NIES, National Institute for Environmental Studies; NIST, National Institute of Standard and Technology; NRCC, National Research Council Canada.

^bConfidence interval, 95%.

4. Conclusions

The preconcentration procedure described in this paper allows cadmium determination in biological materials, whose analysis would be restricted due to poor sensitivity of Flame Atomic Absorption Spectrometry. The system also has low cost, fairly easy operation as well as simplicity and speed.

In open-cell flexible polyurethane foams, at least two windows in each cell must be ruptured for fluids to pass freely through the foam. Utilization of open-cell polyurethane foams in on-line enrichment systems is advantageous because it shows low resistance to the passage of fluids [18]. Thus, the use of minicolumns packed with loaded polyurethane foam in flow systems did not show any overpressure nor swelling as commonly occurs when using other sorbent.

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