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# Flow injection preconcentration system using a new functionalized resin for determination of cadmium and nickel in tobacco samples

Valfredo Azevedo Lemos [*], Cleber Galvão Novaes,
Adriana da Silva Lima, Daniel Rodrigues Vieira

*Laboratório de Química Analítica (LQA), Universidade Estadual do Sudoeste da Bahia,
Campus de Jequié, Jequié-BA 45206-190, Brazil*

## Abstract

A solid-phase extraction method combined with flow injection (FI) on-line flame atomic absorption spectrometry (FAAS) for the determination of cadmium and nickel in tobacco samples is presented. The 2-aminothiophenol functionalized Amberlite XAD-4 (AT-XAD) resin was synthesized by covalent coupling of the ligand with the copolymer through a methylene group. A minicolumn packed with AT-XAD was connected into the automated on-line preconcentration system. Elution of metal ions from minicolumn can be made with $0.50 \, mol \, L^{-1}$ hydrochloric acid solution. With a consumption of $21.0 \, mL$ of sample solution, detection limits (3 s) of 0.3 (Cd) and $0.8 \, \mu g \, L^{-1}$ (Ni) were achieved at a sample throughput of $18 \, h^{-1}$. Enrichment factors (EF) of 99 (cadmium) and 43 (nickel) were obtained compared with the slope of the linear portion of the calibration curves before and after preconcentration. The contents of Cd and Ni in a certified reference material (NIST 1570a, spinach leaves) determined by the present method was in good agreement with the certified value. The developed procedure was also successfully applied to the determination of Cd and Ni in local tobacco samples.
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## 1. Introduction

Cadmium is an element that occurs naturally in the earth's crust. Exposure to cadmium happens mostly in the workplace where cadmium products are made. Food and cigarette smoke are the largest potential sources of cadmium exposure for members of the general population. The cadmium remains in the body for a very long period. Although a lack of nickel has not been found to affect the health of humans, a small amount of nickel is probably also essential for humans. Foodstuffs naturally contain small amounts of nickel. Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. The tobacco plant contains cadmium and nickel, most probably absorbed from the soil, fertilizing products and pesticides. Thus, the determination of trace amounts of these metals in var-

ious matrices samples is very important in several fields, such as environmental analysis, food control and toxicology [1–3].

Due to frequent low concentrations of metals in numerous samples, the determination of these elements generally is associated to preconcentration steps. Moreover, since high levels of major components usually accompany analytes, a separation step is often required. Some enrichment procedures have been developed for metal determination involving different analytical techniques such as precipitation [4], liquid–liquid [5], cloud-point [6,7] or solid-phase extraction [8–11]. Solid-phase extraction (SPE) have been extensively used for separation and determination of trace elements because this approach offers a number of important benefits, such as reducing of disposal costs, achievement of high recoveries and easy recovery of the solid phase. SPE also offers broader range of applications than liquid–liquid extraction due to the large choice of solid sorbents.

Polystyrene-divinylbenzene (PS-DVB) has been largely used as sorbent for extraction of a great number of organic and inorganic substances [8,12]. Commercially available Amber-

* Corresponding author. Fax: +55 73 35289630.
  *E-mail address:* vlemos@uesb.br (V.A. Lemos).

lite XAD-2 and XAD-4 resins are polymeric sorbents based on PS-DVB. The surface of this material is hydrophobic due to hydrocarbon chains. Thus, the retention of trace elements on such materials requires the addition of a ligand to the sorbent. Ligands may be directly introduced to the solid material by physical adsorption. However, the ligand can be gradually leached out of the resin, thereby reducing the lifetime of the impregnated sorbent. A better strategy is to introduce the ligand on the copolymer through a chemical reaction. The functionalization can be made by coupling it to a methylene, azo or other spacer on the matrix [13–15]. This procedure produces a much more stable sorbent, although the resulting metal retention capacities are generally at medium levels [16]. Several ligands immobilized on Amberlite XAD have been successfully used for the on-line flow injection preconcentration and determination of cadmium and nickel [17,18]. Among the ligands incorporated in the solid material through a methylene ($-CH_2-$) group are quinoline-8-ol [19], 4,5-dihydroxy-1,3-benzenedisulfonic acid [20] and 1-(2-pyridilazo)-2-naphtol (PAN) [21]. 2-Aminothiophenol is a very interesting reagent for use in preconcentration procedures of metallic species, because the mercapto group has a strong affinity for transitional metal ions [9]. In view of the good complexing properties of 2-aminothiophenol, it was thought worthwhile to couple this substance with Amberlite XAD-4 through a methylene group.

The purpose of this work was to develop a sensitive and simple method for the determination of cadmium and nickel in tobacco samples by on-line coupling of a FI preconcentration system using an AT-XAD-packed microcolumn. The synthesis and usefulness of this sorbent in an on-line preconcentration system was demonstrated for the first time in this work. The synthesis of the solid support was followed by the study of chemical and hydrodynamic parameters of the system and application of the procedure in real sample analysis.

## 2. Experimental

### 2.1. Apparatus

Absorbance measurements were performed on a PerkinElmer (Norwalk, CT, USA) Model AAnalyst 200 atomic absorption spectrometer equipped with a deuterium background corrector. Hollow-cathode lamps were used as light sources at 228.8 nm for cadmium and 231.1 nm for nickel with a spectral bandpass of 1.0 nm. Deuterium lamp background correction was also used. The flame composition was acetylene (flow rate 2.0 L min$^{-1}$) and air (flow rate 13.5 L min$^{-1}$). Nebulizer flow rate was 5.0 mL min$^{-1}$.

The on-line separation and preconcentration were performed with the FI manifold presented in Fig. 1 [22]. A multichannel peristaltic pump model 204 from Millan (Colombo, Brazil) furnished with silicone tubes was used to delivery all solutions. Four Cole Parmer (Vernon Hills, IL, USA) three way direct lift solenoid valves were used to select preconcentration and elution steps. Solenoid valves were controlled by a microcomputer running software written in Turbo Pascal 4.0. The connections and conduits were made of polytetrafluoroethylene (PTFE) tubing
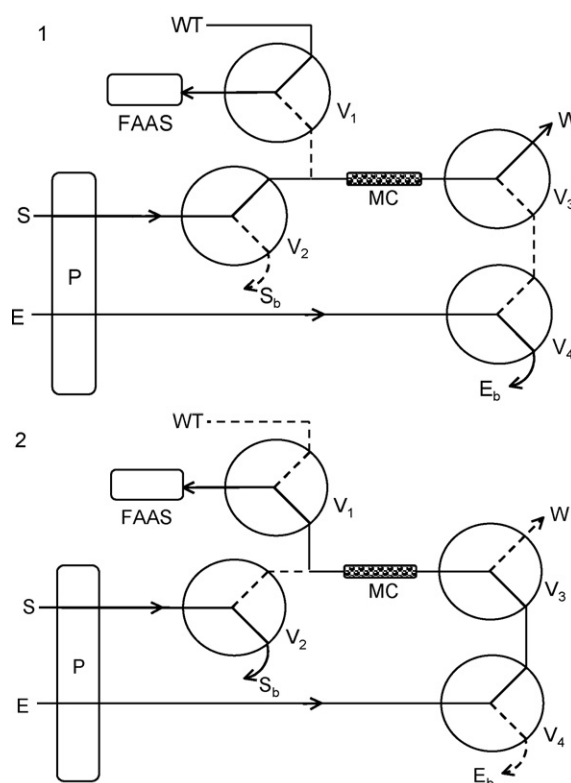


Fig. 1. Schematic diagram of the flow system used to preconcentration and determination of cadmium and nickel by FAAS. S, sample; E, eluent; WT, water; P, peristaltic pump; MC, AT-XAD minicolumn; $V_1$, $V_2$, $V_3$ and $V_4$, solenoid valves; FAAS, flame atomic absorption spectrometer, W, waste; $S_b$, sample back stream, $E_b$, eluent back stream. (1) System in the preconcentration step, solenoid valves on and (2) system in the elution position, solenoid valves off.

(0.50 mm i.d.). Silicone pump tubes were employed for propelling the sample and eluent. All pH measurements were made with a Digimed DM 20 model (Santo Amaro, Brazil) digital pH meter. Digestion of solid samples was carried out in a Parr Instrument 4749 (Moline, IL, USA) Acid Digestion Bomb enclosing a chemically inert Teflon sample cup of 23 mL. Infrared spectra were recorded in an ABB Bomen MB series model MB100 Fourier transform IR spectrometer.

### 2.2. Reagents

Amberlite XAD-4 (specific surface area 330 m$^2$ g$^{-1}$ and bead size 20–60 mesh), a PS-DVB copolymer, was purchased from Aldrich (Milwaukee, WI, USA). Working standard solutions of cadmium and nickel were prepared by stepwise dilution of 1000 μg mL$^{-1}$ stock standard solutions (Merck, Darmstadt, Germany). Hydrochloric and nitric acid solutions used as eluents were prepared by direct dilution from the concentrated solutions (Merck). The functionalized resin AT-XAD was synthesized by using the following reagents: 2-aminothiophenol (Merck), aluminum chloride (Vetec, Rio de Janeiro, Brazil), nitrobenzene (Merck), octanol (Merck) and methylene chloride (Vetec). Acetate (pH 4.8–6.0), borate (pH 7.0–8.0) and ammoniacal (pH 9.0) buffers [23] were used to adjust the pH of the solutions, wherever suitable. In order to evaluate the accuracy of

the method, the following certified reference biological material was analysed: 1570a Spinach Leaves from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Supra-pur HNO$_3$ (65%, w/w, from Merck) was used for sample digestion.

### 2.3. Synthesis of AT-XAD

The sorbent AT-XAD was prepared by a procedure described previously for similar resins [13,14,20]. A 3 g amount of Amberlite XAD-4 was chloromethylated by mixing the copolymer beads with dry 20 mL methylene chloride and 10 mL of octanol. Anhydrous, pulverized aluminium chloride (7 g) was added in small increments to the mixture. The system was refluxed at 90 °C. The reaction was stopped after 24 h and filtered. The resin beads were cleaned with water, acetone, 1:1 (v/v) aqueous hydrochloric acid and again with water. The chloromethylated beads were filtered off and dried for storage. The dried chloromethylated copolymer was suspended in a mixture of 30 mL nitrobenzene and 2.0 g of 2-aminotiophenol. Then the system was refluxed for 72 h at 70 °C under continuous stirring. The mixture was filtered, and the resin was washed twice with 1:1 (v/v) aqueous hydrochloric acid, and water, respectively. The final product was heated in ethanol for 2 h, filtered and dried in air.

To confirm the presence of 2-aminotiophenol in the functionalized polymer, infrared spectra were obtained from AT-XAD and free Amberlite XAD-4. These spectra were studied using the potassium bromide technique. The band around 1610 cm$^{-1}$ resulted from N−H vibrations. A characteristic feature of the functionalized sorbent when compared with free resin is a S−H bond around 2570 cm$^{-1}$. It shows that the reagent was bonded onto the surface of the sorbent after modification.

### 2.4. Analytical procedures

Standard reference material 1570a Spinach Leaves obtained from NIST was used to validate the proposed method. Real cigar and cigarette samples were purchased at supermarkets and street markets from Jequié, Bahia, Brazil. The solid material sample (0.10–0.15 g) was accurately weighed into the 23 mL Teflon cup. Samples were digested by adding 4.0 mL of 1:1 (v/v) nitric acid solution on sample. The acid digestion bomb was heated in a stove at 150 °C for 5 h [24]. Blank samples were prepared in the same way. Sub-samples were spiked with known amount of each analyte. After cooling at room temperature the bomb was opened carefully in a fume cupboard. Sodium hydroxide and an appropriate buffer solution were used to adjust the pH of the final digests. The mixture was finally diluted to 50 or 100 mL by double deionized water. These solutions were analyzed immediately after preparation by introducing them into the preconcentration manifold.

A cylindrically shaped polyvinyl chloride minicolumn (3.50 cm × 4.0 mm i.d.) was packed with 100 mg of the AT-XAD resin. Plastic foams were fixed at both ends of the minicolumn to prevent material losses. The minicolumn was initially washed with 2.0 mol L$^{-1}$ nitric acid solution and deionized water until

the effluent was acid free. It was found that minicolumns could be used repeatedly for at least 500 operational cycles.

A minicolumn packed with AT-XAD was integrated into the FI manifold involving two simple preconcentration and elution steps. The schematic diagram of the flow system is shown in Fig. 1. The preconcentration procedure consisted of the two simple steps. In the sample loading step, the four valves were turned on, so that the sample solution was pumped through the minicolumn and the sample matrix flows towards waste. Meanwhile, a water stream goes to the flame atomic absorption spectrometer (FAAS). After loading, the four solenoid valves were then simultaneously turned off. A stream of eluent pass now through the minicolumn in order to release metal ions directly into the nebulizer of the spectrometer. It was not necessary to recondition the minicolumn at the end of each cycle, since the samples were buffered before preconcentration. Signals were measured as peak height (or maximum absorbance). From preliminary experiments, it was observed that peak height measurement gave better precision that peak area measurement.

## 3. Results and discussion

### 3.1. Optimization of chemical and FI flow conditions

A univariate approach was employed for optimization of the procedure. A known amount of analyte (10 μg L$^{-1}$ for cadmium and 100 μg L$^{-1}$ for nickel) was loaded to the minicolumns. The metals were then eluted and determined by FAAS.

The solution pH is an important parameter in complex adsorption extraction because it affects the complexing reaction between metal ions and 2-aminothiophenol. For this reason, the preconcentration of Cd and Ni from solutions buffered at different pH was studied. The pH was adjusted from 4.8 to 6.0 using sodium acetate–acetic acid buffer, from pH 7.0 to 8.0 using borax–boric acid buffer and to pH 9.0 using ammoniacal buffer. As can be seen in Fig. 2, maximum absorbance occurred at pH ranges of 7.0–8.0. Borate buffer pH 7.5 was chosen as the optimum for subsequent experiments for both metals.
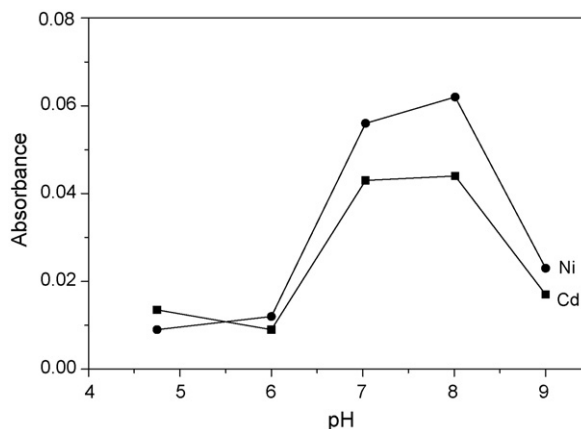


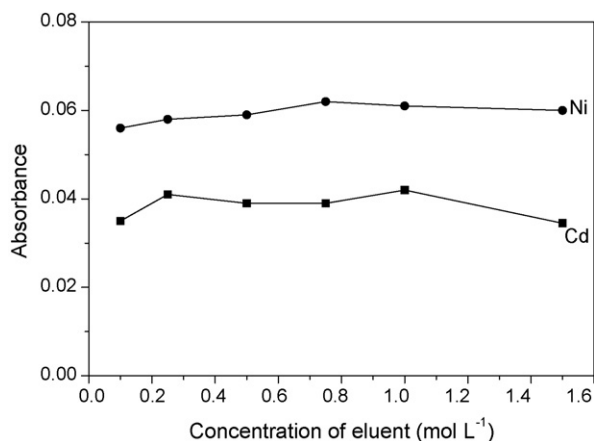Fig. 2. Influence of pH on the retention of cadmium and nickel.

Fig. 3. Influence of concentration of eluent on the retention of cadmium and nickel.

Adsorption of Cd and Ni ions on AT-XAD minicolumn is favorable under neutral and slightly basic conditions. It was expected that an acidic solution would easily elute the sorbed Cd and Ni from the minicolumn. Thus, nitric and hydrochloric acid solutions were tested as the eluent. It was not found any significant difference between the results for the two acids. Hydrochloric acid was chosen for elution. The effect of HCl concentration on the elution of the retained Cd and Ni was examined at various concentrations (0.10–1.50 mol L$^{-1}$). Best results were obtained by using acid concentrations of 0.25–1.50 mol L$^{-1}$ for Cd(II) and 0.25–1.00 mol L$^{-1}$ for Ni(II), according to Fig. 3. Addition of solvents as methanol, ethanol or acetone to acid solutions has not resulted in any increasing of recovery for both metals. The 0.50 mol L$^{-1}$ hydrochloric acid solution was used as eluent for Cd and Ni in all subsequent experiments.

The effect of the sample flow rate was studied using a constant volume (5.0 mL) of solutions containing Cd(II) or Ni(II) ions. These solutions were brought to pH 7.5 and passed through the AT-XAD minicolumn at different flow rates. Flow rates of the sample were studied from 4.0 to 14.0 mL min$^{-1}$. At higher flow rates, backpressure is produced by the minicolumn. Besides, the analytical signal decreased owing to short residence time of ions,

which resulted in an incomplete retention. Otherwise, low flow rates decreases sample throughput resulting in a long time of analysis. In order to improve analytical efficiency, 7.0 mL min$^{-1}$ was chosen as the loading rate for Cd and Ni.

Studies on the influence of preconcentration time for Cd and Ni show that analytical signal increased almost linearly up to 180 s. This indicates that the transfer phase factor is constant within this time interval. Higher preconcentration times could be beneficial to the determination of the samples with lower Cd or Ni concentrations. However, long periods are not interesting for FI preconcentration systems. Preconcentration times of 60 and 180 s were used for the determination of Cd and Ni in cigarette samples.

The influence of eluent flow rate in the elution step was also studied, because it establishes the velocity of acid solution through the minicolumn. Results obtained shown that the analytical signal is maximum at eluent flow rates within the range 3.5–6.0 mL min$^{-1}$. An eluent flow rate of 5.0 mL min$^{-1}$ was selected in subsequent studies, in order to match elution and aspiration (FAAS) flow rates. Considering that the total time of elution was 15 s, the volume of eluent is 1.25 mL.

### 3.2. Sorption capacity

The adsorptive capacity of the AT-XAD sorbent for the retention of cadmium and nickel was also determined. About 100 mg of the resin was equilibrated with 100 mL of 5.0 mg L$^{-1}$ Cd(II) or Ni(II) at pH 7.5. After shaking for 4 h in separate flasks, the mixture was filtered by gravity. Cadmium or nickel were determined in each filtrate by flame atomic absorption spectrometry. The results demonstrated that the sorbent has a sorption capacity of 28.5 and 23.7 μmol g$^{-1}$ of dry resin for cadmium and nickel, respectively.

### 3.3. Performance of the method

Under the optimum conditions, the analytical performance of on-line sorption preconcentration FAAS for Cd and Ni determination is summarized in Table 1. The flow system was operated in a time-based mode. Achieved sampling rate was 48 and 18 h$^{-1}$,

Table 1
Analytical figures of merit for the determination of Cd and Ni by the proposed method

| Element | Cadmium | | Nickel | |
|---|---|---|---|---|
| Preconcentration time (s) | 60 | 180 | 60 | 180 |
| Sample frequency (h$^{-1}$) | 48 | 18 | 48 | 18 |
| Calibration function | $A = 7.00 \times 10^{-3}$ $+ 8.00 \times 10^{-3}C$ | $A = 1.18 \times 10^{-2}$ $+ 2.43 \times 10^{-2}C$ | $A = -2.30 \times 10^{-3}$ $+ 1.46 \times 10^{-3}C$ | $A = 1.31 \times 10^{-2}$ $+ 2.43 \times 10^{-3}C$ |
| Enrichment factor | 33 | 99 | 26 | 43 |
| Concentration efficiency (min$^{-1}$) | 26.4 | 29.7 | 20.8 | 12.9 |
| Transfer phase factor | | 0.90 | | 0.93 |
| Volume of sample (mL) | 7.0 | 21.0 | 7.0 | 21.0 |
| Consumptive index (mL) | 0.21 | 0.21 | 0.26 | 0.49 |
| Limit of detection (μg L$^{-1}$) | 1.1 | 0.3 | 2.1 | 0.8 |
| Limit of quantification (μg L$^{-1}$) | 3.6 | 0.9 | 6.9 | 2.7 |
| Linear range (μg L$^{-1}$) | 2.0–20.0 | 0.5–10.0 | 10.0–200.0 | 2.0–100.0 |
| Precision (%) (Cd 10 μg L$^{-1}$, Ni 100 μg L$^{-1}$) | 4.0 | 3.1 | 5.3 | 1.9 |

$A$, absorbance; $C$, metal concentration (μg L$^{-1}$).

Table 2
Effect of potentially interfering ions on the determination of cadmium ($10\,\mu g\,L^{-1}$) and nickel ($100\,\mu g\,L^{-1}$) by proposed procedure

| Substance | Maximum tolerable amount | |
| --- | --- | --- |
| | Cadmium | Nickel |
| $Al^{3+}$ | $2.0\,mg\,L^{-1}$ | $5.0\,mg\,L^{-1}$ |
| $Cl^-$ | $5.0\,g\,L^{-1}$ | $10.0\,g\,L^{-1}$ |
| $Co^{2+}$ | $1.0\,mg\,L^{-1}$ | $20.0\,mg\,L^{-1}$ |
| $Cu^{2+}$ | $1.0\,mg\,L^{-1}$ | $20.0\,mg\,L^{-1}$ |
| $Fe^{3+}$ | $3.0\,mg\,L^{-1}$ | $5.0\,mg\,L^{-1}$ |
| $K^+$ | $5.0\,g\,L^{-1}$ | $10.0\,g\,L^{-1}$ |
| $Mg^{2+}$ | $1.0\,g\,L^{-1}$ | $0.5\,g\,L^{-1}$ |
| $Na^+$ | $5.0\,g\,L^{-1}$ | $10.0\,g\,L^{-1}$ |
| $SO_4^{2-}$ | $1.0\,g\,L^{-1}$ | $0.5\,g\,L^{-1}$ |
| $Pb^{2+}$ | $1.0\,mg\,L^{-1}$ | $10.0\,mg\,L^{-1}$ |
| $Zn^{2+}$ | $1.0\,mg\,L^{-1}$ | $5.0\,mg\,L^{-1}$ |
| $NO_3^-$ | $5.0\,g\,L^{-1}$ | $10.0\,g\,L^{-1}$ |

when used preconcentration times of 60 and 180 s, respectively, and considering elution time of 15 s. The detection and quantification limits, defined as the concentration of Cd or Ni giving signals equivalent to three and ten times, respectively, the standard deviation of the blank ($n = 12$) were calculated. The precision of the procedure was assessed as relative standard deviation. Regression curves without preconcentration resulted in the following equations: $A = -9.00 \times 10^{-3} + 2.44 \times 10^{-4}C$ (Cd $10$–$1000\,\mu g\,L^{-1}$) and $A = 3.93 \times 10^{-3} + 5.71 \times 10^{-5}C$ (Ni $50$–$3000\,\mu g\,L^{-1}$) for cadmium and nickel, respectively, where $A$ is the absorbance and $C$ is the metal concentration in solu-

Table 3
Determination of cadmium and nickel in tobacco samples ($n = 4$)

| Sample | Cadmium content ($\mu g\,g^{-1}$) | | $R$ (%) | Nickel content ($\mu g\,g^{-1}$) | | $R$ (%) |
| --- | --- | --- | --- | --- | --- | --- |
| | Added | Found[*] | | Added | Found[*] | |
| Cigarette sample 1 | 0.0 | $2.3 \pm 0.1$ | – | 0.0 | <LOQ | – |
| | 2.5 | $4.7 \pm 0.1$ | 96 | 25.0 | $25.2 \pm 0.4$ | 101 |
| Cigarette sample 2 | 0.0 | $2.8 \pm 0.2$ | – | 0.0 | <LOQ | – |
| | 2.5 | $5.5 \pm 0.1$ | 108 | 25.0 | $23.0 \pm 0.9$ | 92 |
| Cigarette sample 3 | 0.0 | <LOQ | – | 0.0 | <LOQ | – |
| | 2.5 | $2.3 \pm 0.1$ | 92 | 25.0 | $26.5 \pm 0.8$ | 106 |
| Cigarette sample 4 | 0.0 | $2.9 \pm 0.1$ | – | 0.0 | <LOQ | – |
| | 2.5 | $5.3 \pm 0.2$ | 96 | 25.0 | $26.2 \pm 1.1$ | 105 |
| Cigarette sample 5 | 0.0 | <LOQ | – | 0.0 | $4.7 \pm 0.1$ | – |
| | 2.5 | $2.4 \pm 0.1$ | 96 | 25.0 | $28.4 \pm 0.4$ | 95 |
| Cigar sample 1 | 0.0 | <LOQ | – | 0.0 | <LOQ | – |
| | 2.5 | $2.3 \pm 0.2$ | 92 | 25.0 | $26.8 \pm 0.9$ | 107 |
| Cigar sample 2 | 0.0 | <LOQ | – | 0.0 | <LOQ | – |
| | 2.5 | $2.5 \pm 0.1$ | 100 | 25.0 | $25.8 \pm 1.2$ | 103 |

Confidence interval 95%; LOQ: limit of quantification; $R$: recovery.

Table 4
Procedures for on-line preconcentration of cadmium and nickel using chemically modified materials

| Sorbent | Reagent | Analyte | EF | $f\,(h^{-1})$ | LOD ($\mu g\,L^{-1}$) | Sample | Detection | Reference |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| AA/PTFE fibers | – | Ni | 23 | 55 | 0.25 | Environmental and biological samples | FAAS | [26] |
| AA/PTFE fibers | – | Cd | 73 | 55 | 0.10 | Environmental and biological samples | FAAS | [27] |
| Silica gel | NBO | Cd | 33 | 20 | 0.10 | CRM and water | FAAS | [28] |
| Rice husks | NaOH | Cd | 72 | 14 | 1.14 | CRM | FAAS | [29] |
| Chitosan | 8-Hydroxyquinoline | Cd | – | – | 0.10 | Water and CRM | FAAS | [30] |
| XAD-2 | 2-Aminothiophenol | Cd | 28 | 51 | 0.89 | Water | FAAS | [9] |
| | | | 74 | 18 | 0.14 | | | |
| Chitosan | SAHQ | Cd | 14 | 26 | 0.20 | Water | FAAS | [31] |
| XAD-2 | Chromotropic acid | Cd | 21 | 51 | 0.40 | CRM | FAAS | [32] |
| XAD-2 | Pyrocatechol | Cd | 22 | 51 | 0.95 | Food | FAAS | [18] |
| | | | 44 | 18 | 0.27 | | | |
| | | Ni | 25 | 51 | 2.30 | | | |
| | | | 48 | 18 | 1.29 | | | |
| XAD-2 | DHB | Cd | 100 | 20 | 0.02 | Vegetables | ICP-OES | [12] |
| | | Ni | 91 | 20 | 0.06 | | | |
| Silica gel | PMTC | Ni | 58 | 36 | 0.06 | Seawater | ETAAS | [33] |
| Chitosan | DHB | Ni | 11 | – | 0.09 | River water and seawater | ICP-OES | [34] |
| XAD-4 | 2-Aminothiophenol | Cd | 33 | 48 | 1.1 | Tobacco | FAAS | This work |
| | | Cd | 99 | 18 | 0.3 | | | |
| | | Ni | 26 | 48 | 2.1 | | | |
| | | Ni | 43 | 18 | 0.8 | | | |

EF, enrichment factor; $f$, sampling frequency; LOD, limit of detection; FAAS, flame atomic absorption spectrometry; ETAAS, electrothermal atomic absorption spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; CRM, certified reference material; AA, acrylic acid; PTFE, polytetrafluoroethylene; NBO, niobium(V) oxide ($Nb_2O_5$–$SiO_2$); XAD-2, Amberlite XAD-2; SAHQ, 5-sulphonic acid 8-hydroxyquinoline; XAD-4, Amberlite XAD-4; DHB, 3,4-dihydroxybenzoic acid; PMTC, 1-(di-2-pyridyl)methylene thiocarbonohydrazide.

tion, in $\mu g\,L^{-1}$. These equations were obtained under optimum conditions of the spectrometer. Enrichment factors (EF) were assessed by comparing the slope of the linear portion of the calibration curve before and after preconcentration. Concentration efficiency (CE) is defined as the product of the enrichment factor and the sampling frequency in number of samples analyzed per hour. Consumptive index (CI) and transfer phase factor were also calculated. Consumptive index reflects the volume of the sample consumed to achieve the EF value. It was calculated by the ratio of the sample volume, in milliliters, and EF. Transfer phase factor is defined as the ratio between the Cd or Ni mass in original sample and that in the concentrate [25].

### 3.4. Evaluation of foreign ions

In order to evaluate the selectivity of the synthesized AT-XAD resin, several interfering substances were tested. Interference from coexisting species in the determination of $10.0\,\mu g\,L^{-1}$ cadmium and $100.0\,\mu g\,L^{-1}$ nickel was studied systematically by the on-line proposed procedure. The tolerable limit of an interfering species was taken as a relative error less than 5%. Potential interfering ions were transition metals which might compete with the Cd or Ni for complexing sites of resin. Typical interfering ions, Co(II), Cu(II), Fe(III), Pb(II) and Zn(II), were chosen to study the interference. The results shown in Table 2 demonstrate that the presence of amounts of species commonly present in tobacco samples have no significant effect on the preconcentration of cadmium and nickel.

### 3.5. Analytical application

Real and SRM samples were analyzed by using 180 s preconcentration time in order to reach the maximum sensitivity. To test the accuracy of the present FI on-line AT-XAD minicolumn preconcentration system, a certified reference material, spinach leaves (NIST 1570a) was analyzed. The contents of Cd $(2.7 \pm 0.1\,\mu g\,g^{-1})$ and Ni $(2.3 \pm 0.2\,\mu g\,g^{-1})$ determined by the present method agreed well with the certified values (Cd $2.89 \pm 0.07\,\mu g\,g^{-1}$ and Ni $2.14 \pm 0.10\,\mu g\,g^{-1}$). The results indicate the effectiveness and accuracy of the procedure.

The feasibility of the proposed method for the determination of Cd and Ni with on-line preconcentration was tested on cigar and cigarette samples. These samples were subjected to dissolution, preconcentration and metal determination using the proposed procedure. The results are listed in Table 3. The recoveries $(R)$ for $2.5\,\mu g\,g^{-1}$ Cd or $25\,\mu g\,g^{-1}$ Ni spiked in the samples studied were calculated to be in the range of 92–108% from Table 3, indicating no interference encountered from these sample matrices. $R$ was calculated as follows: $R(\%) = \{(C_m - C_o)/m\} \times 100$. Where $C_m$ is a value of Cd or Ni in a spiked sample, $C_o$ is a value of metal in a sample and $m$ is the amount of metal spiked. It can be concluded that the described procedure can be successfully applied to these matrices for the preconcentration and determination of cadmium and nickel.

## 4. Conclusion

This procedure demonstrates the feasibility of the determination of cadmium and nickel in tobacco by an automated FI on-line preconcentration system coupled with FAAS using a column packed with AT-XAD. Our methodology was shown to be an effective approach for improving the sensitivity of FAAS Cd and Ni determination.

The system is very simple, rapid, easy to use, fully automated, selective and with a good sensitivity for the determination of Cd and Ni. Table 4 shows a comparison of the proposed procedure with other on-line systems for cadmium and nickel determination using chemically modified sorbents. Analytical features, such as enrichment factor, limit of detection and sampling frequency are comparable to those presented by methods described in the literature.

The results of this study show the potential of this method, which could be applied to monitoring trace Cd and Ni in various biological samples of environmental and toxicological interest.

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