

Cadmium and Lead Cloud Point Preconcentration and Determination in Tobacco Samples by Thermospray Flame Furnace Atomic Absorption Spectrometry

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A espectrometria de absorção atômica com forno tubular na chama (TS-FF-AAS) foi empregada para a determinação de Cd e Pb em diferentes tipos de amostras brasileiras de tabacos após a pré-concentração no ponto nuvem (CP) otimizada por planejamento Doehlert. Para a separação das fases no procedimento por ponto nuvem, Triton® X-114 e 2-(bromo-2-piridilazo)-5-dietilaminofenol (Br-PADAP) foram utilizados como surfactante não iônico e agente complexante, respectivamente. Cádmio e chumbo foram determinados após digestão ácida e pré-concentração por ponto nuvem, sendo que as variáveis otimizadas por planejamento Doehlert foram: volume do agente complexante, volume de Triton® X-114 e pH. Um ponto de máximo foi obtido nas superfícies de resposta para Cd e Pb. Para as determinações dos elementos por TS-FF-AAS, um volume de amostra de 50 µL foi introduzido no tubo de Ni posicionado sobre a chama, usando ar como carregador na vazão de 0,4 mL min⁻¹. Os limites de detecção e os desvios padrão relativos após a combinação de CP e TS-FF-AAS foram de 4,0 e 13 µg kg⁻¹ e 3,1 e 0,7% para Cd e Pb, respectivamente. A exatidão do método proposto foi avaliada realizando-se testes de adição-recuperação e empregando-se material de referência certificado (folhas de chá e folhas de pessegueiro). As recuperações variaram de 93 a 103 e 93 a 107% para Cd e Pb, respectivamente. Todos os resultados obtidos para as amostras dos materiais de referência estão em concordância com os valores certificados a um nível de confiança de 95 ou 99% aplicando-se o teste *t*-Student.

A thermospray flame furnace atomic absorption spectrometer (TS-FF-AAS) was employed to determine Cd and Pb in different Brazilian tobacco samples. Sample pretreatment consisted of acid decomposition and cloud point (CP) preconcentration optimized by Doehlert design. To promote phase separation in the cloud point procedure, polyoxyethylene(8) isoctylphenyl ether (Triton® X-114) and 2-(bromo-2-pyridylazo)-5-diethyl-amino-phenol (Br-PADAP) were used as a nonionic surfactant and a complexing agent, respectively. The variables of the cloud point preconcentration procedure optimized by Doehlert design were: complexing agent volume, Triton X-114 volume, and pH. A response surface maximum point was obtained for Cd and Pb. For TS-FF-AAS, a sample volume of 50 µL was introduced into the hot Ni tube using air carrier at a flow rate of 0.4 mL min⁻¹. The limits of detection and relative standard deviations obtained for Cd and Pb when CP and TS-FF-AAS were associated were 4.0 and 13 µg kg⁻¹, and 3.1 and 0.7%, respectively. Accuracy was checked by addition-recovery experiments, as well as by using two certified reference materials (tea and peach leaves). Cadmium and lead recoveries ranged from 93 to 103 and 93 to 107%, respectively. All results obtained for reference materials were in agreement with certified values at 95 or 99% confidence levels by *t*-Student test.

Keywords: tobacco, acid digestion, cloud point preconcentration, Doehlert design, TS-FF-AAS

Introduction

The relevance of trace metals in biological samples derives from their essentiality, as well as from their potentially toxic effects in living organisms. An example of a toxic trace metal in biological systems that has

no biological function in humans is lead, a cumulative metabolic poison with physiological and neurological effects.¹ Lead has carcinogenic properties and interferes with the resistance to infectious diseases.² Another metal that has no biological function in the human body is cadmium, which, depending on its concentration, can affect all forms of life as well. Chronic exposure to Cd can induce damages to the kidneys, lungs, heart, bones,

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and gonads.² This metal can gradually accumulate in the human body, producing a number of adverse health effects, such as nephrotoxicity and osteotoxicity.¹ The toxicity of Pb and Cd in biological fluids has been reported, especially concerning the determination of safe concentration intervals and overexposure effects. Acceptable concentrations of Pb and Cd in human blood are below 100 and 10 $\mu\text{g L}^{-1}$, respectively, depending on the subject's age and gender; however, individual sensitivity to biological exposure varies.²

Cadmium and lead are present in tobacco samples. Cadmium is the best-studied metal in cigarette smoke and smoking is the main source of Cd intake by humans.³ In contrast, smoking is not the main source of Pb intake by humans, but its contribution has become increasingly relevant. The ability of plants like *Nicotiana tabacum* to accumulate metals is utilized by modern biotechnology to decontaminate soils. However, with respect to tobacco farming for cigarette production, this ability poses a health threat. In fact, toxic metals, such as Al, Cd, Cr, Cu, Pb, Hg, Ni, and Zn, are found in tobacco, cigarette paper and filter, and cigarette smoke. The role of these metals in the pathophysiology of diseases caused by cigarette smoking is poorly understood. Emerging data suggest that the alteration of metal homeostasis in the human body by cigarette smoking plays a crucial role in the genesis of a number of diseases.³

Modern analytical chemistry is characterized by hyphenated analytical techniques that involve the combination of sensitive components to improve detection, as recently proposed by Wu *et al.*⁴ Sometimes, a preconcentration step helps to solve sensitivity problems, such as low analyte concentrations in actual samples or high concentration of matrix interferents present in complex samples, especially in biological ones.⁵

Cloud point extraction (CPE) is a separation and preconcentration procedure that has been extensively applied in the determination of trace metal ions in several matrices.^{6,7} Its main advantages are its low cost, simple experimental procedure, high preconcentration factors, and environmental and personal safety.⁸ Cloud PE is based on the property of most nonionic surfactants in aqueous solutions to form micelles and become turbid when heated to cloud point temperature, above which the micellar solution separates into a small volume surfactant-rich phase and a diluted aqueous phase with surfactant concentration close to the critical micellar concentration (CMC).⁹ Its main limitation is the relatively low partition coefficients of several metal species with determined chelates. However, this can be circumvented with the use of highly hydrophobic ligands.¹⁰

Several analytical techniques, such as molecular absorption spectrophotometry, flame atomic absorption spectrometry (FAAS), inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GF AAS), and inductively coupled plasma optical emission spectrometry (ICP OES), have been used to determine metals in micellar phase with sensitivity in most applications. Although previous results have shown that the FAAS detection limits are incompatible with determination at sub $\mu\text{g L}^{-1}$ levels, depending on the matrix, the detection limits can be improved.¹¹ With this point in view, since Gáspár and Berndt¹¹ proposed thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS), its sensitivity to trace levels for different elements has been improved.¹² The association of CPE procedures and TS-FF-AAS has been used in the last years in the direct determination of some metals in liquid samples.¹³⁻¹⁶

TS-FF-AAS achieves complete sample introduction and increases the concentration of the atoms in the optical path. This technique is based on the atomization of the species through the formation of a thermospray at the end of a ceramic capillary inserted into a hot Ni tube located on the FAAS burner.^{17,18} The tip of the ceramic capillary penetrates the sampling hole, resulting in a very high temperature gradient. The sensitivity for different elements is increased up to two orders of magnitude.^{11,16,17} Slurry sample introduction,^{1,18} direct sample introduction,^{14,19,20} preconcentration methods using CPE,^{12,21} and solid sorbents^{6,22} are some strategies that are applied with TS-FF-AAS.

The aim of this work was to develop an analytical procedure employing Cd and Pb separation and preconcentration by cloud point methodology for their determination in Brazilian tobaccos by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS).

Experimental

Instruments

A Perkin Elmer Model AAnalyst 200 flame atomic absorption spectrometer (Norwalk, USA) equipped with a deuterium lamp background correction system was used. Electrodeless discharge lamps were used in the determination of Cd and Pb. The wavelength and spectral band pass were set at 283.3 and 0.7 nm for Pb and 228.8 and 0.7 nm for Cd. An acetylene flow rate of 2.5 L min^{-1} was used with an air flow rate of 10.0 L min^{-1} . The FAAS instrumental parameters were adjusted according to the manufacturer's recommendations.

In the TS-FF-AAS determinations were used a system with one six-channel peristaltic pump (Ismatec,

Labortechnik Analytik, Glattbrugg-Zürich, Switzerland) furnished with Tygon tubes, a lab-made commuting injector, and a thermospray flame furnace unit, which included the ceramic capillary (0.5 mm i.d., 2.0 mm o.d., and 100 mm in length) and a Ni tube (10 cm). The tube was located on the burner, laid on four ceramic fixed pins of a lab-made stainless steel support and could be moved in and out of the flame. To reach the proper atomization temperature for Cd and Pb inside the tube, six 2-mm diameter holes were drilled on the bottom of the tube. Another hole was drilled at 90° to the bottom holes for inserting the thermospray capillary. The capillary tip was set about 1 mm inside the tube furnace. The manifold was assembled with 0.5-mm i.d. PTFE tubing.¹³

The samples were prepared using a muffle furnace (Quimis, Q318M, Diadema, SP, Brazil), a hot plate (Tecnal, 1E085 Piracicaba, SP, Brazil), a centrifuge (Janetzi T32, Berlin, Germany), a domestic microwave oven (Panasonic, São Paulo, SP, Brazil), and a pHmeter (Digimed DM20 São Paulo, SP, Brazil).

Reagents and solutions

All solutions were prepared using analytical grade reagents (Merck, Darmstadt, Germany) and distilled and deionized water (Druckfester Mischbett-Wasservollentsalzer, DI800, Munich, Germany). The laboratory glassware was kept overnight in 10% v/v nitric acid solution, rinsed with deionized water, and dried in a dust-free environment before use.

Reference solutions of Cd and Pb were prepared daily by diluting 1000 mg L⁻¹ stock solution with 1% v/v HNO₃ solution. A 1.0 mmol L⁻¹ solution of Br-PADAP in 5.0% (m/v) Triton® X-114 (Sigma-Aldrich, St. Louis, MO, USA) solution was prepared by dissolving 36.0 mg of 2-(bromo-2-pyridylazo)-5-diethyl-amino-phenol (Br-PADAP) in water and adding 5.0 g of nonionic surfactant. The volume was completed to 100.0 mL with distilled-deionized water. A buffer solution with pH 9 was prepared by mixing 50.0 mL of 0.1 mol L⁻¹ H₃BO₃/KCl and 21.5 mL of 0.1 mol L⁻¹ NaOH. The pH was adjusted using 0.5 mol L⁻¹ NaOH and the volume was completed to 100.0 mL with distilled-deionized water. The viscosity of the micellar phase was reduced using a 0.1 mol L⁻¹ HNO₃ in ethanol 90% (v/v) diluent solution.

Samples

Different Brazilian tobacco samples (regular cigarettes, tobacco rolls, and straw cigarettes) manufactured by different companies bought at a local market in Belo

Horizonte, Minas Gerais, Brazil were analyzed using TS-FF-AAS.

The accuracy of the proposed method was checked with standard reference materials, tea leaves (GBW 08505) and peach leaves (GBW 08501), produced by the Research Center for Eco-Environmental Sciences (Beijing, China).

Ash and wet digestion procedure

A mass of 500 mg of tobacco samples was mineralized at 450 °C for 6 h, until a white ash was obtained. The residue was treated with 2.0 mL of concentrated nitric acid and evaporated to dryness before heating at 450 °C for 30 min. The cooled residue was moistened with water and dissolved in 1.0 mL of concentrated hydrochloric acid and water. After cooling, the colorless solution was made up to 25.0 mL with water.²³

As previously mentioned, all solutions were prepared using analytical grade reagents and distilled and deionized water.

Cloud point extraction procedure for the determination of Cd and Pb by TS-FF-AAS

The preconcentration procedure addition sequence for Cd and Pb was as follows: 10.0 mL of sample, 1.0 mL buffer solution pH 9.0, Br-PADAP solution (1.0 mmol L⁻¹), and Triton® X-114 solution 5.0% (m/v). The solution was placed in a domestic microwave oven at 10% of the maximum power to accelerate the formation of micelles in the cloud point preconcentration procedure and to prevent sample loss, as discussed by Bezerra *et al.*¹⁰

The separation of the micellar phase from the aqueous phase was accelerated by centrifuging the solution for 10 min at 2500 rpm. The solution was cooled in an ice bath and kept in it for 15 min. The micellar phase became viscous and the aqueous phase was removed by inverting the container. In the last step, 0.5 mL of diluent was added to the separated micellar phase. After the addition of the nitric acid/ethanol solution, 50 µL of the micellar phase was introduced into the spectrometer through the sampling system and the analytical signals were recorded in integrated absorbance.

Optimization procedure for Cd and Pb cloud point extraction applying Doehlert design

Based on previously reported data,^{8,24} some experiments were made using PAN (piridylazonaftol) and Br-PADAP as complexing agents in the cloud point preconcentration

procedure. In TS-FF-AAS, the best atomic absorbance signals were obtained employing Br-PADAP. Thus, the optimization study was performed with Br-PADAP.

The preconcentration cloud point procedure was optimized using a Doehlert design in association with response surface methodology (RSM). A Doehlert matrix is a second-order design that can be drawn with two, three, or more variables or factors.^{25,26} It allows identifying critical points (maximum, minimum, and saddle points) at each step of the optimization process and consists of an experimental design in which a set of points is uniformly distributed in a spherical lattice (in a case of three variables). The whole experimental domain is assayed with a minimum number of experiments following a sequential approach. For a k number of factors, $(k^2 + k + 1)$ experiments are required.²⁷ According to the Doehlert design for three variables, the factors pH and final concentration of the Br-PADAP solution were studied at five levels. The final concentration of the Triton® X-114 5.0% (m/v) solution was studied at three levels. Table 1 shows the design matrix for the optimization experiments of these variables with laboratory values, along with coded values in parentheses. The pH was studied in the 7.0-11.0 range. The final concentration of Br-PADAP was studied using volumes ranging from 50 to 450 μL , whereas the final concentration of the Triton® X-114 5.0% (m/v) solution was studied using volumes from 50 to 1050 μL .

The experimental data were processed using the Statistica® software.²⁸

Results and Discussion

CP preconcentration optimization of the experimental conditions using Doehlert design

The CP preconcentration conditions were optimized using 50.0 $\mu\text{g L}^{-1}$ Cd and Pb reference solutions. Air was used as a carrier to avoid the pronounced dispersion observed at the solution-carrier interface.^{19,20} The flow rate used to introduce 50 μL of the micellar solution into the hot Ni tube was 0.4 mL min^{-1} . Flow rates higher than 0.65 mL min^{-1} may reduce the sensitivity, because the residence time of the liquid in the heated capillary tip is too short for evaporation to occur.⁹

In the Doehlert design, variables pH, complexing agent, and surfactant volumes were optimized according to the coded and real values described in Table 1. This table also presents the integrated absorbance and peak height values for Cd and Pb metal ions. Figures 1 and 2 present the Cd and Pb surface responses, respectively, and the relationship between the pH and the Triton® X-114 volume. The statistical program allowed plotting two-dimensional graphs. Maximum points were obtained for all surface responses, including those obtained with

Table 1. Doehlert design and integrated absorbance for Cd and Pb after CPE + TS-FF-AAS optimization procedure

Experiment	Volume Br-PADAP/ μL	pH	Volume Triton X-114**/ μL	Cd Integrated absorbance/(s^{-1})	Pb Integrated absorbance/(s^{-1})	Cd Peak Height	Pb Peak Height
1	450 (1)	9 (0)	550 (0)	5.41	2.84	1.30	0.37
2	350 (0.5)	8 (-0.5)	50 (-0.817)	1.76	1.14	0.33	0.34
3	350 (0.5)	8 (-0.5)	1050 (0.817)	1.81	2.32	0.25	0.24
4	350 (0.5)	10 (0.5)	50 (-0.817)	6.08	2.26	1.16	0.55
5	350 (0.5)	10 (0.5)	550 (0.817)	6.28	2.11	1.22	0.49
6	250 (0)	7 (-1)	550 (0)	4.16	1.57	1.30	0.44
7	250 (0)	9 (0)	550 (0)	4.87	3.47	1.17	0.73
7	250 (0)	9 (0)	550 (0)	4.86	3.39	1.19	0.73
7	250 (0)	9 (0)	550 (0)	4.86	3.21	1.17	0.73
7	250 (0)	9 (0)	550 (0)	4.66	3.57	1.17	0.72
8	250 (0)	11 (1)	550 (0)	1.10	0.40	0.04	0.08
9	150 (-0.5)	8 (-0.5)	50 (-0.817)	0.68	1.65	0.26	0.40
10	150 (-0.5)	8 (-0.5)	1050 (0.817)	5.42	1.33	1.12	0.24
11	150 (-0.5)	10 (0.5)	50 (-0.817)	1.50	1.96	0.05	0.44
12	150 (-0.5)	10 (0.5)	1050 (0.817)	2.56	1.26	0.40	0.30
13	50 (-1)	9 (0)	550 (0)	1.74	2.55	0.32	0.56

* $10^{-3} \text{ mol L}^{-1}$ Br-PADAP solution; **Triton X-114 5.0% (m/v).

Br-PADAD. Thus, the relationship between the pH and the Triton® X-114 solution was chosen to demonstrate the results. Figures 1 and 2 illustrate the maximum points. The application of Lagrange's criterion²⁷ to each equation gave the Cd and Pb critical values. For the optimized cloud point extraction procedure, it was used a volume of 245 μL of complexing agent solution (Br-PADAP), 765 μL of Triton® X-114 solution, and pH 9 for Cd, while for Pb, 295 μL of Br-PADAP, 580 μL of Triton® X-114, and pH 9 were used. These values were used considering the interactions of the three variables. These experimental conditions were applied in further experiments for determination of Cd and Pb in tobacco samples. The final concentrations of the Br-PADAP solution were 1.8×10^{-2} and 2.1×10^{-2} mmol L^{-1} , and for the Triton® X-114 solution, 0.36 and 0.31% m/v, for Cd and Pb, respectively.

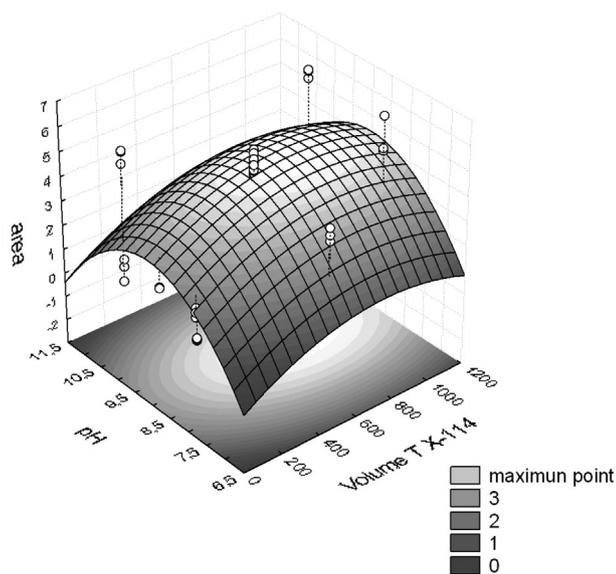


Figure 1. Surface response for peak area integrated absorbance of Cd [pH vs. Vol TX (Triton® X-114)].

Analytical characteristics

Figures of merit for Cd and Pb measurements were obtained by TS-FF-AAS using the optimized experimental conditions. The results are presented in Table 2. The limits of detection (3 standard deviations of the blank/slope) and quantification (10 standard deviations of the blank/slope) were determined from 10 blank readings. The Cd and Pb LOD's found using CP preconcentration and TS-FF-AAS were 4.0 and 13 $\mu\text{g kg}^{-1}$, respectively. The detectability improvement factors for Cd and Pb were 62 and 158, respectively, when comparing the proposed method (CPE + TS-FF-AAS) with conventional FAAS. The

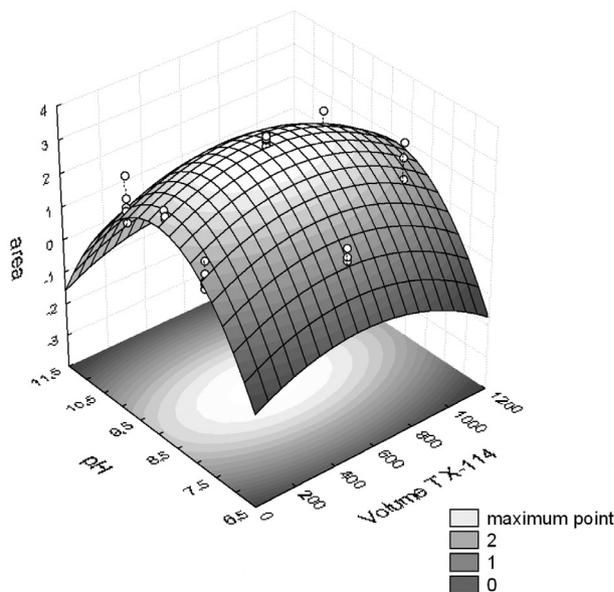


Figure 2. Surface response for peak area integrated absorbance of Pb [pH vs. Vol TX (Triton® X-114)].

repeatability for Cd and Pb, 3.1 and 0.7%, respectively, was determined by successive measurements of the standard solutions ($25 \mu\text{g L}^{-1}$). The linear dynamic range varied from 0.08 to $25 \mu\text{g L}^{-1}$ for Cd, and from 0.26 to $250 \mu\text{g L}^{-1}$ for Pb.

Table 2. Analytical characteristics of the Cd and Pb measurements by TS-FF-AAS

	Cd	Pb
Linear dynamic range/ $(\mu\text{g L}^{-1})$	0.08-25	0.26-250
Linear correlation coefficient	0.9985	0.9979
R.S.D./(%)	3.1	0.7
LOD/ $(\mu\text{g kg}^{-1})$	4.0	13.0
LOQ/ $(\mu\text{g kg}^{-1})$	14.0	41.0
Improvement factor	62	158

Accuracy and recovery studies

To evaluate the accuracy of the developed procedure, Cd and Pb were determined in the two standard reference materials (Peach leaves-GBW08501 and Tea leaves-GBW08505). The results are presented in Table 3. No difference was observed for Cd and Pb in either sample by *t*-Student test at 95% confidence level, except for the Pb content in tea leaves, which was in agreement at 99% confidence level.

Recovery of Cd and Pb in different tobacco samples was evaluated in triplicate at two levels by adding 2.5 and $5.0 \mu\text{g L}^{-1}$ of both elements to commercial samples. The results are given in Table 4. Recovery ranged from 93 to

Table 3. Cadmium and lead determinations in two standard reference materials by TS-FF-AAS (mean \pm standard deviation, $n = 4$, $P = 0.05$)

	Certified values/ $(\mu\text{g g}^{-1})$		Obtained values/ $(\mu\text{g g}^{-1})$	
	Cd	Pb	Cd	Pb
Tea leaves- GBW08505	0.032 \pm 0.005	1.06 \pm 0.10	0.029 \pm 0.002	1.45 \pm 0.22*
Peach leaves- GBW08501	0.018 \pm 0.008	0.99 \pm 0.08	0.019 \pm 0.009	1.23 \pm 0.39

* $P = 0.01$.**Table 4.** Recovery experiments for Cd and Pb in different tobacco samples ($n = 3$)

Sample	Cd			Pb		
	Added/ $(\mu\text{g L}^{-1})$	Found/ $(\mu\text{g L}^{-1})$	Recovery/ (%)	Added/ $(\mu\text{g L}^{-1})$	Found/ $(\mu\text{g L}^{-1})$	Recovery/ (%)
regular	2.5	10.6	98.2	2.5	5.1	94.6
regular	5.0	12.9	94.2	5.0	7.4	93.1
straw	2.5	15.1	102.5	2.5	22.7	92.5
straw	5.0	17.6	101.3	5.0	25.2	96.5
roll	2.5	16.0	95.6	2.5	30.3	105.3
roll	5.0	18.3	93.2	5.0	32.9	106.6

107% for both analytes. No matrix effects were observed in the optimized procedure for the regular tobacco samples.

Determination of Cd and Pb in tobacco samples

After conventional acid digestion combining ash and wet digestion and optimized cloud point extraction using Br-PADAP as a complexing agent, commercial tobacco samples were analyzed using TS-FF-AAS. Cadmium and lead were not directly detected in tobacco acid digests by FAAS. Results are shown in Table 5. The samples named regular are common pack cigarettes bought at local shops, as previously mentioned. The found concentrations ranged from 0.148 to 0.380 $\mu\text{g g}^{-1}$ for Cd, and from 0.568 to 3.51 $\mu\text{g g}^{-1}$ for Pb. Regular HR cigarette presented the lowest Cd value, while CPC straw cigarette gave the highest Pb value. The standard deviations obtained are suitable, taking into account the various steps of the proposed procedure. It can be seen in Table 5 that the standard deviations were higher for Cd and Pb at lower concentrations than those obtained for tobacco samples with the highest analyte concentrations. The Cd and Pb LOD's obtained in this study were similar to literature values.^{17,21} Tarley *et al.*⁶ found a lower value for Cd employing TS-FF-AAS in combination with a minicolumn preconcentration system using multiwall carbon nanotubes. However, the method proposed here gave satisfactory results with good accuracy for the investigated samples.

Table 5. Determination of Cd and Pb in tobacco samples by TS-FF-AAS (mean \pm standard deviation, $n = 3$)

Tobacco samples	Cd/ $(\mu\text{g g}^{-1})$	Pb/ $(\mu\text{g g}^{-1})$
DR regular	0.227 \pm 0.060	0.740 \pm 0.077
DG regular	0.313 \pm 0.097	3.00 \pm 0.04
HR regular	0.148 \pm 0.036	3.00 \pm 0.02
C regular	0.228 \pm 0.012	3.07 \pm 0.05
T regular	0.213 \pm 0.028	2.99 \pm 0.04
CPP straw	0.349 \pm 0.005	0.568 \pm 0.040
CPC straw	0.345 \pm 0.069	3.51 \pm 0.03
CPVJ straw	0.221 \pm 0.009	3.11 \pm 0.05
CPD straw	0.242 \pm 0.063	3.08 \pm 0.05
FRF roll	0.380 \pm 0.020	0.769 \pm 0.040
FRM roll	0.213 \pm 0.032	3.06 \pm 0.14
FRf roll	0.235 \pm 0.027	3.14 \pm 0.05
FRG roll	0.189 \pm 0.022	2.94 \pm 0.05

Conclusions

Cadmium and lead were determined in tobacco samples by TS-FF-AAS technique after acid digestion and optimized cloud point preconcentration using Br-PADAP as a complexing agent. The optimization of the cloud point preconcentration conditions by Doehlert design improved the sensitivity for determination of Cd and Pb using a small number of experiments and employing reduced reagent

volumes. The association of TS-FF-AAS with cloud point preconcentration led to a gain about 62-158-fold higher than that obtained by FAAS. The proposed procedure may be applicable to other elements present in low concentrations in tobacco samples and to quality control.

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