

Highly improved sensitivity of TS-FF-AAS for Cd(II) determination at ng L⁻¹ levels using a simple flow injection minicolumn preconcentration system with multiwall carbon nanotubes

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A new method for cadmium determination at ng L⁻¹ levels is described. The method is based on the on-line coupling of a flow preconcentration system using multiwall carbon nanotubes (MWCNT) as sorbent with TS-FF-AAS determination. Cadmium preconcentration was at pH 4.9 onto an MWCNT minicolumn (30 mg) for 2 min at a 5.0 mL min⁻¹ flow rate. The elution step is performed by using 0.5 mol L⁻¹ HNO₃ and the cadmium desorbed is directly pumped to a TS-FF-AAS. All experimental parameters that play important roles in system performance were evaluated and optimized by means of fractional factorial designs and response surface methodology. The excellent characteristics of MWCNT as sorbent, mainly owing to its high surface area, make it possible to obtain a preconcentration factor of 51-fold, thus improving the detection and quantification limits in TS-FF-AAS, 11.4 and 38.1 ng L⁻¹, respectively. When the flow preconcentration system, FI-TS-FF-AAS, was compared with FAAS alone, an increase in the sensitivity of 640-fold was obtained. The calibration graph was linear with a correlation coefficient higher than 0.999 from 38.1 to 1250 ng L⁻¹. Repeatability of the measurements ($n = 10$), assessed as relative standard deviation (RSD), was found to be 6.5 and 2.1% for cadmium concentrations of 100 and 1000 ng L⁻¹, respectively. Important parameters to characterize the flow preconcentration system were also evaluated, the consumption index being 0.196 mL, the concentration efficiency 25.5 min⁻¹ and the sample throughput 20 samples per hour. In order to demonstrate the accuracy of the system, addition and recovery studies in water samples (mineral water, tap water and river water) and cigarette samples were carried out. Moreover, for the same purpose, cadmium was determined in certified biological materials (Bovine Liver and Rye Grass), giving an average result in close agreement with the certified value.

1. Introduction

Routine metal determinations by spectroanalytical techniques have commonly been carried out by flame atomic absorption spectrometry (FAAS), owing to its ease of operation and its low acquisition and operating costs compared with inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace atomic absorption spectrometry (GFAAS).¹ However, as is well known, FAAS provides detection limits that are incompatible with levels actually required for metal determinations at sub µg L⁻¹ levels. Besides, depending on the nature of the matrices, the detection limits of the technique are increased. Hence, prior sample treatment methods, based on separation/preconcentration, are applied, aiming to remove interferences and/or to improve the sensibility of the techni-

que. Among these methods, solid phase separation/preconcentration systems using flow injection are often chosen owing to their attractive features, allowing fewer possibilities of contamination, high preconcentration factors, good analytical precision, good sample throughput and ease of coupling to spectroanalytical techniques.² It is well documented from the literature that recent papers focus on the development of preconcentration systems coupled on-line to FAAS due to the attractive features of the technique.³⁻⁵ In this context, more sensitive methods could be obtained if preconcentration systems were coupled to a recent modification of atomic absorption spectrometry, thermospray flame atomic absorption spectrometry (TS-FF-AAS), a naturally more sensitive technique than FAAS. Since TS-FF-AAS was developed, in 2000,⁶ many efforts have been expended towards its application in the analytical field. Slurry sample introduction, direct sample introduction of fluids, such as milk, fruit juices and beer, as well as preconcentration methods, are some examples applying TS-FF-AAS.⁷⁻⁹

The success of sorbent preconcentration systems coupled to spectroanalytical techniques depends on the features of solid sorbent. In this way, the choice of sorbent is directed to those

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materials with suitable selectivities, high chemical stabilities and high available surface areas. Many available materials for solid phase preconcentration, such as chelating polymeric resins, polyurethane foam and functionalized inorganic materials (silica gel and alumina), have been used.^{10–13} The analytical protocols for the development of the sorbent preconcentration system using these materials are carried out basically from three approaches, where the materials are chemically modified with chelating agents acting as supports, used without loading with chelating agents or in an unloaded form but requiring the addition of chelating agents into the flow system. The adsorption of chelating agents loaded onto sorbents or their inclusion in the flow system enhances the selectivity of the preconcentration procedures. However, in some situations the lifetime of those sorbents loaded with chelating agents is not very high,¹¹ while those flow systems containing additional lines promote an excessive consumption of chelating agents. In this context, sorbents containing high surface areas and, of course, with high adsorptive capacities, make it possible to obtain an efficient, selective and simpler flow preconcentration system. In this sense, carbon nanotubes, a novel carbon material, in two common configurations, single wall carbon nanotubes (SWCNT) and multiwall carbon nanotubes (MWCNT), present excellent features as sorbents for preconcentration purposes due to their large specific surface areas and hexagonal arrays of carbon atoms.¹⁴ Although such materials have generated a great deal of interest, owing to their exceptional chemical and physical properties, being promising materials for many applications, including polymer reinforcement,¹⁵ catalyst support¹⁶ and in the building of electrochemical sensors,¹⁷ their application for preconcentration purposes is still rare, particularly if one considers their great potential. The few investigations of carbon nanotubes potential as a sorbent for metal ions that have been published are for the trace rare earth metals, cadmium, manganese, copper and nickel, using ICP-OES and FAAS, where most of the preconcentrations were performed in the off-line mode.^{18–20}

The aim of this work was to develop a new, simple and sensitive sorbent flow preconcentration system for cadmium determination at ng L^{-1} levels, combining the good performance of TS-FF-AAS with the excellent properties of carbon nanotubes as sorbent. This combination has not been reported in the literature, at least to our knowledge. All optimizations of the method were performed by using fractional factorial design and response surface methodology, which presents advantages over the univariate method, including a lower number of assays and, mainly, improved optimization when the effect of one variable depends on the others. The feasibility and accuracy of the proposed method was investigated by analyzing water and cigarette samples as well as certified reference materials.

2. Experimental

2.1. Apparatus

A Shimadzu AA-6800 flame atomic absorption spectrometer (Shimadzu, Tokyo, Japan), equipped with a hollow cathode lamp for cadmium and with a deuterium lamp for background

correction, was used. The hollow cathode lamp was operated at 8.0 mA and the wavelength was set at 228.8 nm. The flame composition was operated with an acetylene flow rate of 3.0 L min^{-1} and air flow rate of 10.0 L min^{-1} . The thermospray apparatus was composed of a pure nickel tube (J&J Ethen, 52070, Aachen, Germany) of length 10 cm and 2.5 cm i.d., containing 6 holes of 2.5 mm i.d. facing the burner allowing flame penetration inside the tube. The ceramic capillary (10 cm in length, 0.5 mm i.d. and 2.0 mm o.d.), used for transporting samples towards the nickel tube, was made of non-porous Al_2O_3 ceramic (Friatec, Mannheim, Germany). The nickel tube was kept above the burner head by means a home-made holder. The flow preconcentration system was constructed using a peristaltic pump from Ismatec, Model IPC (Ismatec IPC-08, Glattbrugg, Switzerland) furnished with Tygon[®] tubes to propel all sample and reagent solutions while a home-made injector commutator made of Teflon[®] was used to select the preconcentration/elution steps. The transport lines were made of PTFE tubes of 0.8 mm i.d. The morphological characteristics of the carbon nanotubes were evaluated using a JEOL JMT-300 scanning electron microscope (SEM) (Tokyo, Japan). Photographs were obtained by applying an electron acceleration voltage of 20 kV after the carbon nanotubes were covered with a thin layer of gold. X-ray diffraction spectra were acquired from a Shimadzu XRD 6000 X-ray diffractometer (Kyoto, Japan) operated with incident X-rays ($\lambda = 1.54060 \text{ \AA}$) with the 2θ angle varying between 5 and 80° . The surface area of MWCNT was obtained by using the BET technique using ASAP 2010 equipment (Micromeritics). The sample pH was measured by a Handylab 1 Schott pH meter (Stafford, UK). The certified reference materials, as well as the cigarette samples, were decomposed using a microwave oven (Milestone, Sorisole, Italy).

2.2. Reagents and solutions

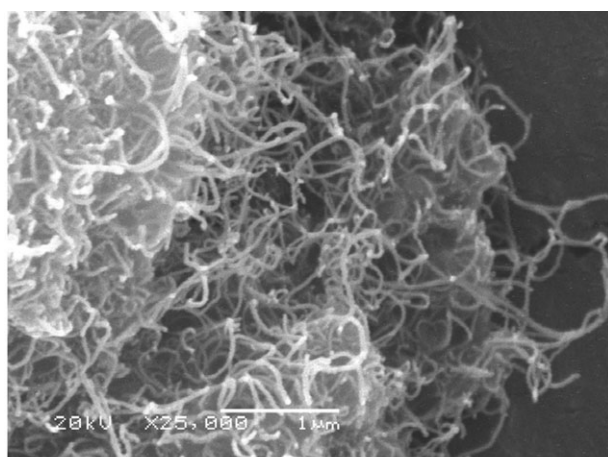
All solutions used in this work were prepared with analytical grade chemical reagents as well as with water obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). Before use, laboratory glassware was kept overnight in a 10% (v/v) HNO_3 solution, aiming to avoid any metal contamination. Cadmium standard solutions were prepared daily by appropriate dilution of a 1000 mg L^{-1} cadmium solution (Merck, Darmstadt, Germany).

Acetate and phosphate buffer solutions were prepared from their respective sodium salts purchased from Merck without further purification, by dissolving appropriate masses in pure water followed by pH adjustment to the desired value with sodium hydroxide and/or nitric acid solutions. In the acid sample decomposition procedures using microwave radiation, concentrated HNO_3 and 30% (v/v) H_2O_2 (Merck, Darmstadt, Germany) were used throughout this work. Prior to use the HNO_3 was purified with a sub-boiling system (Milestone, Sorisole, Italy).

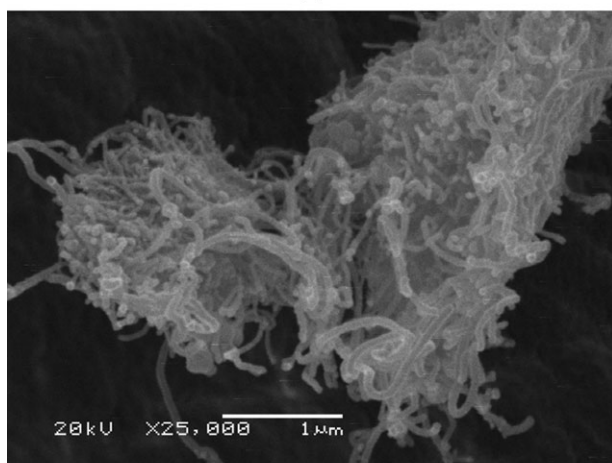
The carbon nanotubes used in this work were MWCNT (purity >93%, 10–40 nm i.d. and 5–20 μm long) kindly supplied by CNT Co., Ltd. (Korea). This material consists of carbon atom layers forming sheets rolled in a cylindrical format. As MWCNT present characteristics of an apolar

sorbent, its use was possible after a prior treatment with concentrated HNO_3 . This treatment, beyond ensuring the elimination of the metallic catalyst used in MWCNT synthesis, makes possible the formation of binding sites on the MWCNT surface.²¹ The treatment was performed according to the literature with minor modifications,¹⁴ and comprises the dispersion of 500 mg of MWCNT in 30 mL of concentrated HNO_3 followed by heating for 1 h at 120 °C under reflux. Next, successive washings with pure water were carried out to remove excess acid (to neutral pH). Finally, the material was dried at 100 °C and stored until use. MWCNT were inserted into a minicolumn (6.0 × 1.0 cm i.d.) made of poly(vinyl chloride) (PVC) containing glass wool at both ends so that sorbent losses during the preconcentration/elution steps could be avoided.

Fig. 1 displays a SEM image of the raw MWCNT and of MWCNT oxidized with concentrated HNO_3 . As one can see, MWCNT was open-ended, thus indicating that acid treatment is successful. This supposition is in accordance with literature data,²² which also reports that the main functional group created after the oxidation process is the carboxylic group, which can participate as an ion exchanger in the adsorption



(a)



(b)

Fig. 1 Scanning electron micrographs of raw MWCNT (a) and MWCNT oxidized with concentrated HNO_3 (b). The images were amplified 25000 times.

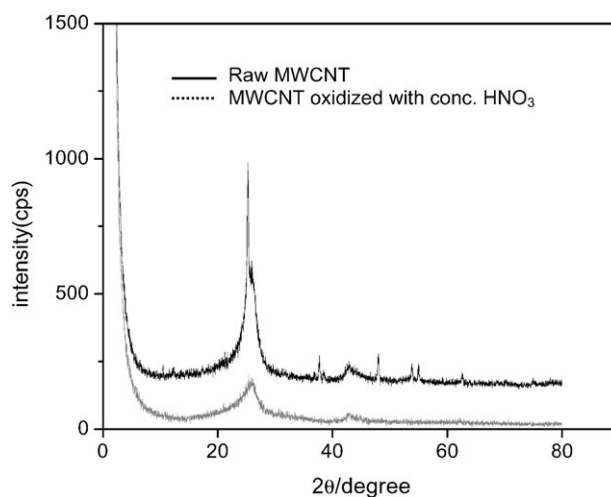


Fig. 2 X-ray diffractograms of MWCNT.

process. Fig. 2 exhibits X-ray diffractograms of the raw material and MWCNT oxidized with concentrated HNO_3 with two characteristic diffraction peaks at $2\theta = 25$ and 45° attributed, respectively, to the inter-layer spacing of carbon layers and within the carbon layers.²² As MWCNT are considered to be multiple layers of carbon sheets in a cylindrical format, depending on the cylinder diameter the inter-layer spacing can vary from 3.4 to 3.9 Å. Thus, the stronger peak, verified for those MWCNT treated with concentrated HNO_3 in relation to raw MWCNT, can be explained due to transformation of amorphous carbon, provoking some degree of graphitization and, as a consequence, changes in the inter-layer spacing of the carbon layers. The surface area for the oxidized MWCNT was found to be $146.2 \text{ m}^2 \text{ g}^{-1}$.

2.3. Flow preconcentration system coupled to TS-FF-AAS

The flow preconcentration manifold was operated with only two lines. In the first one, standard or sample solution, buffered (pH = 4.9) with 0.002 mol L^{-1} acetate buffer, is pumped towards the minicolumn packed with 30 mg of MWCNT at a 5.0 mL min^{-1} flow rate for 2.0 min, as shown in Fig. 3. The remaining solution flows directly to waste, while eluent solution ($0.5 \text{ mol L}^{-1} \text{ HNO}_3$) flows towards the TS-FF-

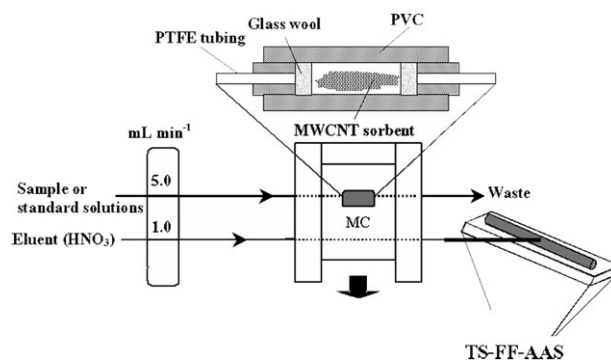


Fig. 3 Diagram of flow system for cadmium preconcentration onto MWCNT.

AAS detector. Following preconcentration, the commutator position is manually changed to its second position, for the elution step, thus locating the minicolumn in the flow of eluent (1.0 mL min^{-1}), which displaces cadmium ions to the TS-FF-AAS. Absorbance signals were taken as peak height for establishing the relation between analytical concentration and analytical signal.

2.4. Sample preparation

The feasibility of the procedure developed was checked by analysis of water and cigarette samples as well as with certified reference materials (CRM 281 and CRM 1577b). River water samples were collected in polypropylene bottles from a river near Alfenas city. Samples were filtered through $0.45 \mu\text{m}$ cellulose acetate membranes under vacuum and the pH was adjusted to 4.9 with 0.002 mol L^{-1} acetate buffer. Mineral and tap water samples were treated in similar ways, but without the filtering procedure. All water samples were used in the recovery tests.

Two certified reference materials [Bovine Liver (CRM 281) and Rye Grass (CRM 1577b)] and cigarette samples were analysed. About 200 mg of samples were digested with 10 mL concentrated HNO_3 and 4 mL 30% (v/v) H_2O_2 using two heating steps in a microwave oven: 5 min at 400 W and 5 min at 700 W. After digestion, the solutions were heated on a hot plate to near dryness. Finally, the residues, previously cooled at room temperature, were dissolved in distilled/de-ionised water and the pH was adjusted to 4.9 with 0.002 mol L^{-1} acetate buffer. Blank solutions were also prepared for each sample.

2.5. Optimization

The optimization of the proposed method was performed using multivariate statistical techniques, which is more efficient and precise if compared with the univariate method. Factorial design has become a helpful tool in determining the effects of factors associated to the analytical response. Moreover, as far is known, the optimum response value for one factor studied often depends on the levels of other factors investigated in the study. This dependence of factors, also known as the interaction effect, frequently occurs in the optimization of analytical procedures. The only way of measuring these interaction effects is using optimization strategies such as factorial design. Commonly, two level factorial design (2^K , where K is the number of factors) is used for testing the effects of each factor as well as the effects of interactions; however, when many factors may play an important role in the system, a fractional factorial design, such as the one reported here, is indicated. The fractional factorial design is based on a fraction of a full factorial design and comprises 2^{K-p} experiments where p is the size of the fraction. In the present study, a 2^{5-1} fractional factorial design was used with the aim of determining the importance of five factors in the analytical response. The definitions of the factors and their levels are summarized in Table 1. From the establishment of these significant factors in the study, the final optimization was carried out using the Doehlert design in association with response surface methodology. The analyses of experimental assays were processed using the STATISTICA software package (StatSoft, Tulsa, USA).

Table 1 Factors, levels and results [absorbance (peak height) and efficiency of sensitivity] obtained for the 2^{5-1} fractional factorial design. The generator of fractional factorial design is $I = 12345$

Factors	Levels	
	(-) Low	(+) High
1. pH	3.2 ^a	7.0 ^b
2. Buffer concentration (BC)/mol L ⁻¹	0.001	0.01
3. Preconcentration flow rate (PFR)/mL min ⁻¹	2.5	5.0
4. Eluent concentration (EC)/mol L ⁻¹	0.5	1.0
5. Type of eluent (TE)	HNO_3	HCl

Runs	1	2	3	4	5	Absorbance (peak height)	Efficiency of sensitivity (ES)
1	—	—	—	—	+	0.082/0.081	0.0205/0.020 25
2	+	—	—	—	—	0.028/0.031	0.007/0.007 75
3	—	+	—	—	—	0.034/0.035	0.0085/0.008 75
4	+	+	—	—	+	0.039/0.037	0.00975/0.009 25
5	—	—	+	—	—	0.07/0.071	0.0350/0.0355
6	+	—	+	—	+	0.024/0.027	0.0120/0.0135
7	—	+	+	—	+	0.054/0.051	0.0270/0.0255
8	+	+	+	—	—	0.033/0.029	0.0165/0.0145
9	—	—	—	+	—	0.092/0.089	0.023/0.022 25
10	+	—	—	+	+	0.027/0.030	0.006 75/0.0075
11	—	+	—	+	+	0.042/0.045	0.0105/0.011 25
12	+	+	—	+	—	0.037/0.038	0.009 25/0.0095
13	—	—	+	+	+	0.069/0.071	0.0345/0.0355
14	+	—	+	+	—	0.029/0.026	0.0145/0.0130
15	—	+	+	+	—	0.042/0.037	0.021/0.01850
16	+	+	+	+	+	0.025/0.028	0.0125/0.0140

^a $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$. ^b $\text{KH}_2\text{PO}_4-\text{NaOH}$.

3. Results and discussion

Table 1 summarizes the 16 assays, carried out in duplicate, containing the combinations of a 2^{5-1} fractional factorial design. It should be noted that the assays were performed in random order, which is consistent with good statistical technique. The last column of signals (5) was built from the generator of fractional factorial design, being $I = 12345$. Hence, the signals of column (5) were obtained by multiplying the signals from columns (1), (2), (3) and (4). All assays were performed by using a cadmium solution at a concentration of 150 ng L^{-1} , setting the sampling volume at 10 mL . Both absorbance (peak height) and efficiency of sensitivity (ES) were evaluated as analytical responses. This latter is obtained from the ratio between absorbance and the time in minutes required in the preconcentration step, thus this response also takes into account the sample throughput of the proposed method, very important in flow preconcentration systems.

The significance of factors as well as their interactions were checked from analysis of variance (ANOVA) and are represented by a Pareto Chart using confidence intervals at the 95% level, defined by the vertical line (Fig. 4). Horizontal bars higher than the vertical line establish the significance of factors. Therefore, as verified, the factor most statistically significant was the sample pH for both analytical responses. The negative effect estimated for sample pH indicates that, by

increasing its level within the experimental domain (3.2 to 7.0), the retention of cadmium ions onto the MWCNT surface is decreased. Concerning the buffer concentration (BC), a similar behaviour was verified. The interaction $\text{pH} \times \text{BC}$ is highly significant; however the effect estimated presents a positive value, thus indicating that, by simultaneously increasing their levels, higher analytical responses can be achieved. The preconcentration flow rate (PFR) showed, as expected, an opposite behaviour regarding both analytical responses where the effects estimated were -7.24 and 31.41 , respectively, for absorbance and efficiency of sensitivity. The mass transfer of cadmium ions to the MWCNT surface is significantly affected at the upper level of preconcentration flow rate tested (5.0 mL min^{-1}), probably owing to a slow kinetics retention of cadmium ions onto the material within the factor levels studied. However, if one considers the ES as an analytical response, higher PFR promotes increases in the analytical response. Thus, in order to establish a compromise between sample throughput and absorbance, PFR was set at 5.0 mL min^{-1} . Higher values were not tested to avoid leakages in the mini-column system owing to resultant overpressure. The last factors investigated, eluent concentration (EC) and type of eluent (TE) were not statistically significant within the experimental domains. Therefore, HNO_3 at a concentration of 0.5 mol L^{-1} was adopted as the eluent solution. This acid was chosen because of its ease of purification with regard to hydrochloric acid. Sample pH and buffer concentration were simultaneously optimized using Doehlert design made in duplicate (Table 2). This two-level full factorial comprises 7 different assays, which makes possible evaluation of the fit of a quadratic model for these experimental results. Eqn (1) represents the relationship between absorbance (peak height) and the factors studied.

$$\text{Abs} = -0.088 + 0.053\text{pH} - 0.0052\text{pH}^2 + 8.341\text{BC} - 1144.87\text{BC}^2 - 0.9034\text{pHBC} \quad (1)$$

Analysis of variance (ANOVA) (Table 3) was employed for evaluation of the significance of the quadratic model represented by eqn (1). There are two possibilities for attesting the significance of the proposed model. The $\text{MS}_{\text{lof}}/\text{MS}_{\text{pe}}$ ratio, also known as the ratio between two variances, can be used, comparing sources of variations through the F -test. When the $\text{MS}_{\text{lof}}/\text{MS}_{\text{pe}}$ ratio is higher than the tabled critical F value,

Table 2 Doehlert design and results obtained for the flow preconcentration system for cadmium onto MWCNT coupled to TS-FF-AAS

Runs	pH^a	BC^a	Absorbance (peak height)	Predicted value using the quadratic model
1	4.1 (-0.5)	0.0050 (0.866)	0.039/0.037	0.035
2	5.1 (0.5)	0.0050 (0.866)	0.040/0.041	0.037
3	5.6 (1)	0.0028 (0)	0.049/0.047	0.046
4	5.1 (0.5)	0.0005 (-0.866)	0.051/0.053	0.049
5	4.1 (-0.5)	0.0005 (-0.866)	0.045/0.046	0.044
6	3.6 (-1)	0.0028 (0)	0.045/0.042	0.040
7	4.6 (0)	0.0028 (0)	0.052/0.050	0.048

^a The values in parentheses are the codified values from the Doehlert design for two factors while the first value represents the real values of the factors. BC = buffer concentration ($\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$).

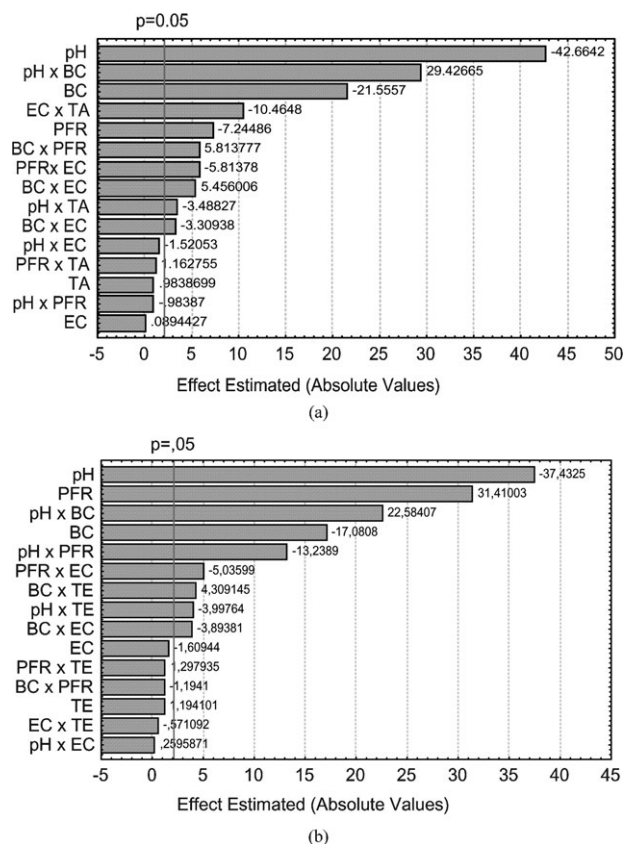


Fig. 4 Pareto Chart involving the effect estimated for the factors and their interactions. (a) Response as absorbance (peak height); (b) response as efficiency of sensitivity (ES). BC = buffer concentration; PFR = preconcentration flow rate; EC = eluent concentration; TA = type of acid.

Table 3 Analysis of variance (ANOVA) from the design shown in Table 2^a

Effect	Sum of squares (SS)	Degrees of freedom (DF)	Mean of squares (MS)	F-test	Probability level (<i>p</i>)
pH	0.000 055	1	0.000 055	28.546 15	0.001 072
pH ²	0.000 037	1	0.000 037	19.055 56	0.003 293
BC	0.000 181	1	0.000 181	93.592 59	0.000 027
BC ²	0.000 080	1	0.000 080	41.241 30	0.000 360
pH × BC	0.000 008	1	0.000 008	4.286 16	0.077 182
Lack of fit (lof)	0.000 006	1	0.000 006	3.361 99	0.109 371
Pure error (pe)	0.000 014	7	0.000 002		
Total SS	0.000 342	13			

^a $R^2 = 0.941 48$ and R^2 adjusted = 0.90491.

the model presents lack of fit and naturally is not suitable. In this way, as the MS_{lof}/MS_{pe} ratio of 3.362 is smaller than that tabled critical $F_{1,7}$ value of 5.59, it indicates that the quadratic model does not present lack of fit: in other words, the model is significant. Another way to confirm this test is from the comparison of the *p* (probability level) value of statistic test with significance level α , commonly employed as 0.05. Thus, if $p \geq \alpha$, the source of variation studied, here lack of fit, is not significant. As is shown in Table 3, the probability level (0.109) for lack of fit is higher than 0.05, thus corroborating with the *F*-test in establishing the significance of the quadratic model with confidence at the 95% level. In addition, the experimental results are in good agreement with the values predicted by the quadratic model (Table 3). The resulting response surface of the quadratic model is displayed in Fig. 5, which indicates optimum values for pH and buffer concentration ($CH_3COOH-CH_3COONa$) at 4.9 and 0.002 mol L⁻¹, respectively. The optimum pH value achieved also confirms the majority presence of carboxylic groups produced on the MWCNT surface after acid treatment, once the adsorption pH (4.9) is near to the pK_a values for carboxylic groups, despite the MWCNT being treated with concentrated HNO_3 also to show hydroxyl and ketones groups.

3.1. Interference studies

Interference experiments were carried out under optimized conditions using a cadmium solution at 150 ng L⁻¹ concentra-

$$\text{Abs} = -0.088200737858076 + 0.053814480829355 \cdot \text{pH} - 0.0052499999999999 \cdot \text{pH}^2 + 8.34135732138 \cdot \text{BC} - 1144.8726394379 \cdot \text{BC}^2 - 0.90340628599628 \cdot \text{pH} \cdot \text{BC}$$

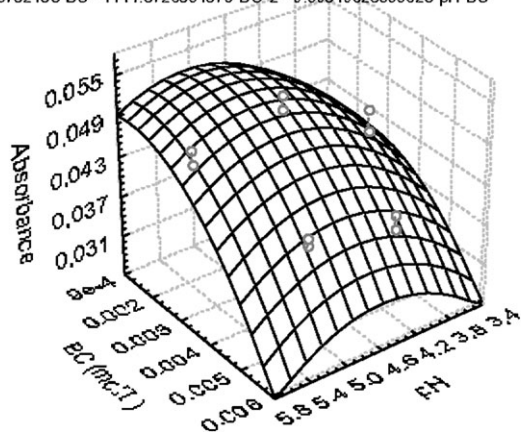


Fig. 5 Surface response obtained from Doehlert design employed for optimization of sample pH and buffer concentration.

tion. Here, the interference, evaluated individually, was considered when foreign ions cause a change in the cadmium signal alone ($\pm 10\%$). The results obtained for several foreign ions are summarized in Table 4. Metallic ions, such as Fe^{3+}

Table 4 Results obtained for several foreign ions in the flow pre-concentration system coupled to TS-FF-AAS for cadmium determination

	Concentration of foreign ions	Recovery of cadmium analytical signal (%) ^a
Zn^{2+}	200 $\mu\text{g L}^{-1}$	102.5
	1 mg L^{-1}	102.5
	5 mg L^{-1}	80.7
Pb^{2+}	500 $\mu\text{g L}^{-1}$	97.5
	1 mg L^{-1}	79.0
	30 mg L^{-1}	77.8
Co^{2+}	200 $\mu\text{g L}^{-1}$	80.7
	1 mg L^{-1}	121.8
	5 mg L^{-1}	119.0
Al^{3+}	200 $\mu\text{g L}^{-1}$	107.6
	1 mg L^{-1}	63.0
	5 mg L^{-1}	33.5
Cu^{2+}	200 $\mu\text{g L}^{-1}$	103.8
	1 mg L^{-1}	73.4
	5 mg L^{-1}	32.8
Ni^{2+}	200 $\mu\text{g L}^{-1}$	123.4
	1 mg L^{-1}	101.9
	5 mg L^{-1}	32.8
Mn^{2+}	200 $\mu\text{g L}^{-1}$	112.7
	1 mg L^{-1}	96.6
	50 mg L^{-1}	104.2
Mg^{2+}	1 mg L^{-1}	115.8
	10 mg L^{-1}	39.5
Fe^{3+}	200 $\mu\text{g L}^{-1}$	98.3
	1 mg L^{-1}	110.9
	5 mg L^{-1}	109.2
Cr^{3+}	30 $\mu\text{g L}^{-1}$	109.2
	500 $\mu\text{g L}^{-1}$	110.9
	2 mg L^{-1}	121.8
Ca^{2+}	1 mg L^{-1}	67.2
	10 mg L^{-1}	71.7

^a Recovery percentage for the cadmium analytical signal using a cadmium solution at 150 ng L⁻¹.

and Mn^{2+} , are sufficiently tolerated at high concentration at mg L^{-1} levels. The majority of other metals tested promote a decrease in the cadmium signal recovery only at high concentration and these results might be related to the competition between cadmium ions and interferent ions for those sites of MWCNT. Concerning the effect of Cr^{3+} and Co^{3+} ions, positive interferences were noted. As chromium and cobalt species present a high affinity for oxygen atoms, oxides are easily formed and, as consequence, can exert influence on the thermodynamic equilibrium of cadmium after atomization into nickel tube heated by a flame, thus increasing the analytical signal.²³ In spite of these behaviours, it is important to remember that the high interferent/analyte ratio tested is not usually found in real samples. Moreover, when analyzing real samples from different matrices the presence of co-existing metal ions may cause an antagonistic effect regarding the interference studies carried out here. As will be demonstrated later, the present proposed system allowed the interference-free determination of cadmium ions in different types of sample.

3.2. Analytical features

The proposed method, under the optimum conditions, provided a linear analytical curve ranging from 38.1 to 1250.0 ng L^{-1} with a correlation coefficient higher than 0.999. The calibration equation obtained by flow preconcentration coupled to TS-FF-AAS was $\text{Abs} = 3.74 \times 10^{-6} + 2.10 \times 10^{-4} [\text{Cd} (\text{ng L}^{-1})]$, while that built without the preconcentration system was $\text{Abs} = 9.16 \times 10^{-5} + 4.12 \times 10^{-6} [\text{Cd} (\text{ng L}^{-1})]$. The enhancement of TS-FF-AAS sensitivity by inserting the preconcentration step with MWCNT is attested to by the preconcentration factor (PF). This important parameter was calculated as the ratio between the slopes of analytical curves with and without the preconcentration step, with a 51-fold increase in the sensitivity being found. Also, the great usefulness of the on-line coupling of the preconcentration system with TS-FF-AAS was attested by comparing it with the sensitivity of FAAS. In this way, as the analytical curve of FAAS was $\text{Abs} = 2.40 \times 10^{-3} + 3.28 \times 10^{-7} [\text{Cd} (\text{ng L}^{-1})]$, a notable increase in sensitivity of 640-fold was found. The low limits of detection (11.4 ng

L^{-1}) and quantification (38.1 ng L^{-1}) were defined according to IUPAC,²⁴ and were based on three and ten times the standard deviation of ten measurements of the blank solution. The precision of the method assessed as relative standard deviation (RSD) of ten independent preconcentration cycles using 100 and 1000 ng L^{-1} cadmium solutions was 6.5 and 2.1%, respectively. The entire preconcentration/elution cycle requires 3 min, thus the sample throughput was found to be 20 per hour.

Other parameters recommended as criteria for the evaluation of the efficiency and reliability of the on-line preconcentration systems were also evaluated.²⁵ Concentration efficiency (CE) defines the sensitivity enhancement of the technique using the preconcentration system operated at 1 min. As a PF of 51 was obtained using a preconcentration time of 2 min, CE became 25.5 min^{-1} . The consumption index (CI) establishes the volume expressed in millilitres necessary to attain a unit of PF. Hence, CI was found to be 0.196 mL. According to Table 5, the proposed method provides a lower limit of detection as well as a comparable or better PF, CE and CI regarding the results obtained from other on-line preconcentration systems for cadmium determination by spectroanalytical techniques (except GFAAS) (Table 5). Owing to the notable performance of the preconcentration system, a significant improvement in the TS-FF-AAS sensitivity was achieved, as has already been seen with several methods dedicated to on-line coupling of a preconcentration system to TS-FF-AAS.

3.3. Accuracy of the proposed method and analysis of samples

The preconcentration method developed was validated by analysis of water samples as well as samples submitted to acid decomposition. In this study, the cadmium content was determined by employing external calibration. The accuracy of the proposed method was evaluated through recovery tests analyzing water and cigarettes samples (Table 6) and certified reference materials (Table 7). As one can see, the accuracy was assured in all instances for samples analyzed based on a recovery percentage varying from 94 to 107%. In addition, the cadmium content obtained by the developed method is in

Table 5 Comparison of different flow preconcentration systems coupled to spectroanalytical techniques including the proposed method (FI-TS-FF-AAS)^a

Sorbent	Chelating agent	PF	CI/mL	CE/ min^{-1}	LD/ $\mu\text{g L}^{-1}$	Technique	Ref.
Amberlite XAD-2	2-Aminothiophenol	28	0.21	24	0.89	FAAS	26
Amberlite XAD-4	<i>O,O</i> -Diethylthiophosphate (DDTP)	20	0.90	4	1.0	FAAS	27
Knotted reactor	1-(2-Thiazolylazo)- <i>p</i> -cresol (TAC)	23	0.43	11.5	0.04	FAAS	28
Acrylic acid grafted PTFE fibres	—	73	0.10	97.3	0.10	FAAS	29
$\text{Nb}_2\text{O}_5\text{-SiO}_2$	—	33	0.43	16.5	0.10	FAAS	30
Rice husks modified with NaOH	—	72.4	0.33	18.1	1.14	FAAS	31
Polyurethane foam	2-(2-Benzothiazolylazo)-2- <i>p</i> -cresol (BTAC)	41	0.17	41	0.27	FAAS	32
Amberlite XAD-2	Pyrocatechol	22	0.23	19	0.95	FAAS	33
SiO_2	DPTH	86	0.07	57	1.1	ICP OES	34
SiO_2	TS	62	0.19	25	4.3	ICP OES	34
Fullerene	Ammonium pyrrolidinedithiocarbamate (APDC)	11	0.13	14.6	0.1	TS-FF-AAS	35
Polyurethane foam	<i>O,O</i> -Diethylthiophosphate (DDTP)	5	0.4	6.0	0.12	TS-FF-AAS	36
MWCNT	—	51	0.196	25.5	0.01	TS-FF-AAS	This work

^a PF = preconcentration factor; CI = consumption index; CE = concentration efficiency; DPTH = 1,5-bis(di-2-pyridyl)methylene thiocarbonylhydrazine; TS = methylthiosalicylate.

Table 6 Recovery results for the accuracy evaluation in the cadmium determination by FI-TS-FF-AAS

Samples	Cadmium concentration added (ng L ⁻¹)	Cadmium concentration found ^a (ng L ⁻¹)	Recovery (%)
Mineral water	0	<LD ^b	—
	100	107.0 ± 7.1	107
Tap water	0	<LD	—
	100	94.5 ± 5.9	94
River water	0	<LD	—
	100	94.0 ± 6.9	94
Cigarette sample/ µg g ⁻¹	0	0.581 ± 0.006	—
	0.20	0.823 ± 0.06	105

^a The results are expressed as mean value ± standard deviation based on three replicates ($n = 3$). ^b LD = limit of detection.

Table 7 Analysis of certified reference materials using the FI-TS-FF-AAS method

Certified reference materials	Certified value/µg g ⁻¹	Value found ^a /µg g ⁻¹
Rye Grass CRM281	0.120 ± 0.003	0.122 ± 0.010
Bovine Liver CRM 1577b	0.50 ± 0.03	0.49 ± 0.02

^a The results are expressed as mean value ± standard deviation based on three replicates ($n = 3$).

accordance (confidence interval at 95% using *t*-test) with those values defined by the certified reference materials. These results demonstrate that the sorbent preconcentration system coupled to TS-FF-AAS for cadmium determination is not affected by potential interferences in different types of matrices.

4. Conclusions

The use of MWCNT as a sorbent in a flow preconcentration system coupled to TS-FF-AAS is shown to be a good alternative for the development of an analytical protocol aimed at cadmium determination at ng L⁻¹ levels. MWCNT provides a useful means of concentrating cadmium using a flow system, since a very low overpressure was observed. Moreover, owing to the good characteristics of MWCNT, such as a large specific surface area, implying a high adsorptive capacity, cadmium preconcentration is interference-free, as demonstrated by analysis of different matrices, which is very interesting for routine laboratories involved in trace element analysis. Beyond the satisfactory selectivity achieved without chelating agents, the method developed is characterized by simplicity with respect to already existing preconcentration procedures, using only two lines in a flow system. Finally, it is important to point out that the method developed was able to expand the usefulness of MWCNT in sorbent processes, in this case using a flow system, which has not yet been reported in the literature, and also exhibits an excellent configuration, joining the advantages of flow preconcentration to those of TS-FF-AAS. The result is an improvement in TS-FF-AAS detectability, attested to by a lower detection limit compared with other preconcentration

systems coupled to spectroanalytical techniques, mainly ICP-OES, FAAS and also TS-FF-AAS.

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