On-line simultaneous pre-concentration procedure for the determination of cadmium and lead in drinking water employing sequential multi-element flame atomic absorption spectrometry

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An on-line pre-concentration system for the sequential determination of cadmium and lead in drinking water by using fast sequential flame atomic absorption spectrometry (FS-FAAS) is proposed in this paper. Two minicolums of polyurethane foam loaded with 2-(6-methyl-2-benzothiazolylazo)-orcinol (Me-BTAO) were used as sorptive pre-concentration media for cadmium and lead. The analytical procedure involves the quantitative uptake of both analyte species by on-column chelation with Me-BTAO during sample loading followed by sequential elution of the analytes with $1.0 \, mol \, L^{-1}$ hydrochloric acid and determination by FS-FAAS. The optimisation of the entire analytical procedure was performed using a Box–Behnken multivariate design utilising the sampling flow rate, sample pH and buffer concentration as experimental variables.

The proposed flow-based method featured detection limits (3σ) of 0.08 and $0.51 \, \mu g \, L^{-1}$ for cadmium and lead, respectively, precision expressed as relative standard deviation (RSD) of 1.63% and 3.87% ($n = 7$) for cadmium at the $2.0 \, \mu g \, L^{-1}$ and $10.0 \, \mu g \, L^{-1}$ levels, respectively, and RSD of 6.34% and 3.26% ($n = 7$) for lead at the $5.0 \, \mu g \, L^{-1}$ and $30.0 \, \mu g \, L^{-1}$ levels, respectively. The enrichment factors achieved were 38.6 and 30.0 for cadmium and lead, respectively, using a sample volume of $10.0 \, mL$. The sampling frequency was 45 samples per hour. The accuracy was confirmed by analysis of a certified reference material, namely, SRM 1643d (Trace elements in natural water). The optimised method was applied to the determination of cadmium and lead in drinking water samples collected in Santo Amaro da Purificação City, Bahia, Brazil.

Keywords: on-line pre-concentration; sequential determination; cadmium, lead; drinking water; flame atomic absorption spectrometry

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1. Introduction

The determination of cadmium and lead in surface waters is usually required considering their toxic effects and hazards on human health and the environment [1,2]. To this aim, the most commonly used analytical techniques involve electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS). The flame atomic absorption spectrometry (FAAS) technique is cheaper, but it does not have sensitivity for determination of trace amounts. Thus, several pre-concentration procedures have been developed over the past few years encompassing liquid-liquid (micro)extraction [3–6], cloud point extraction [7], coprecipitation [8] and sorption onto knotted reactors [9]. For enrichment of trace metals in a vast number of matrices [10,11] chelation solid-phase pre-concentration has been widely exploited [12,13]. An important factor that regulates the extraction efficiency in solid phase extraction (SPE) is the capacity and selectivity of the chelating reagent for the complexation of target metal ions. Chelators involving the pyridylazo and thiazolylazo moieties have been proven particularly suitable for extraction of lead and cadmium at trace level concentrations [14–16]. As compared to batchwise counterparts, on-line flow-based systems are more advantageous for implementation of sample processing as a result of their inherent automation, precise handling of sample and reagents in an entirely enclosed environment, and minimum consumption of chemicals, which is in good agreement with the principles of green chemistry [17]. The selection of the appropriate pre-concentration method in a flow-based mode is not always straightforward and depends on the required analytical performance, the potential interfering species in the sample matrix, the robustness of the flow manifold, the sample availability, the compatibility of reagents and solvents with the detector device and the intended application of the flow set-up, that is, in-situ monitoring or on-line/at-line laboratory assays [18].

In the present paper, a flow-injection sorptive pre-concentration method is proposed for the on-line enrichment and sequential determination of cadmium and lead in drinking water samples by employing fast sequential multi-element flame atomic absorption spectrometry (FS-FAAS). The system is based on sorption of cadmium and lead ions onto two minicolums of polyurethane foam loaded with 2-(6-methyl-2-benzothiazolylazo)-orcinol (Me-BTAO). The optimisation of the analytical procedure was performed by using a second order multivariate design capitalised on the Box-Behnken model [19].

2. Experimental

2.1 *Instrumentation*

The experiments were performed using a Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) multi-element flame atomic absorption spectrometer equipped with a fast sequential module system and a conventional pneumatic nebuliser (FS-FAAS). A multi-element silver, cadmium, lead and zinc hollow cathode lamp was operated under the conditions suggested by the manufacturer at a current of 10.0 mA. The most sensitive wavelengths for cadmium (228.8 nm) and lead (217.0) nm were used with bandwidths of 0.5 nm and 1.0 nm for cadmium and lead, respectively. The flame was composed of acetylene (flow rate: 2.0 L min^{-1}) and air (flow rate: 13.5 L min^{-1}) and the burner height was fixed at 13.5 mm. The nebuliser uptake flow rate was maintained throughout within the range 5.5 and 6.0 mL min^{-1}.
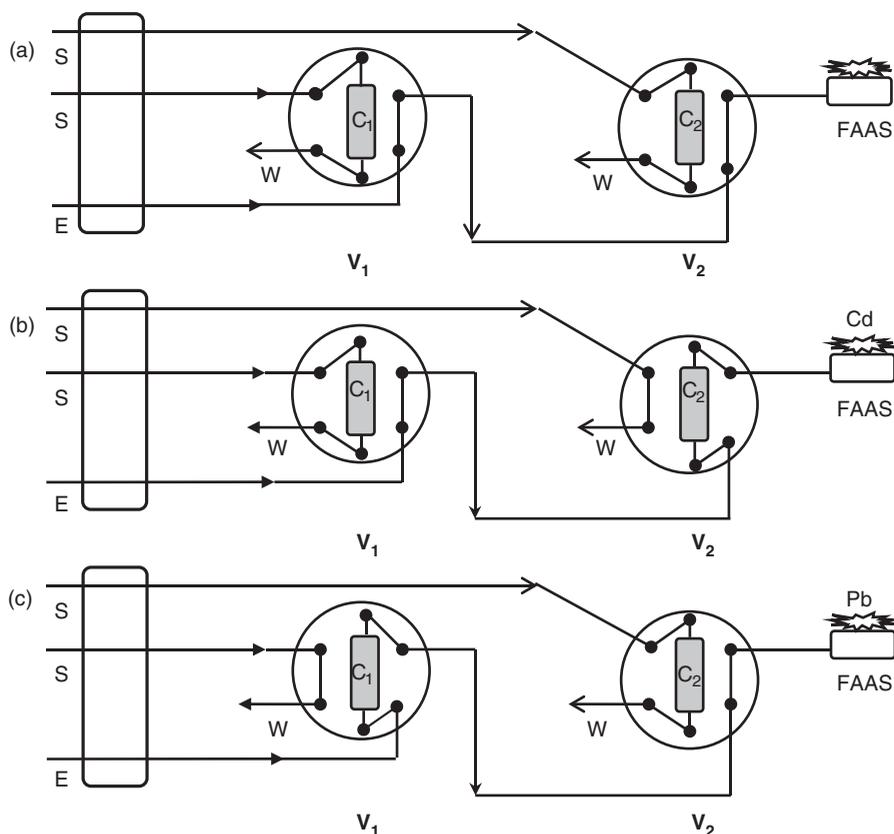
Figure 1. Schematic diagram of the online pre-concentration system for sequential determination of cadmium and lead and detection by FS-FAAS. S, sample; E, eluent; W, waste; P, peristaltic pump; C, column; V_1 and V_2, load-injection valves; (a) sampling position; (b) elution position for Cd; (c) elution position for Pb; FAAS, flame atomic absorption spectrometer.

The flow injection system assembled is showed in Figure 1. An Alitea C-6 XV (Stockholm, Sweden) peristaltic pump equipped with Tygon tubes was employed to propel the sample and eluent. The system is furnished with two rotary injection valves in series (V1 and V2, Rheodyne 5041, Cotati, CA, USA) equipped each with a sorptive pre-concentration column in the position of the injection loop. The flow network is built with PTFE tubing of 0.5 mm i.d and PVC connectors.

2.2 *Chemicals, reagents and materials*

All chemicals used in this work were of analytical reagent grade.

Ultrapure water (18.2 MΩ cm^{-1}) was obtained from EASY pure Milli-Q Millipore RF system (Barnstedt, Dubuque, IA, USA).

Stock standard solutions of cadmium and lead (Merck) at a concentration level of 1000 μg mL^{-1} each were used to prepare working standard solutions by appropriate dilution with 1% (v/v) nitric acid.

A stock TRIS buffer solution was prepared by dissolving 12.1 g of tris-(hydro-xymethylamine)-methane (Merck) in 100.0 mL of deionised water, and the pH adjusted to the required value with concentrated hydrochloric acid.

A Me-BTAO solution (0.04% (w/v)) was prepared by dissolving 0.04 g of 2-(6-methyl-2-benzothiazolylazo)-orcinol in 100.0 mL of absolute ethanol (Merck).

Commercial polyether-type polyurethane foam (PUF, Atol, Simoes Filho, Bahia, Brazil), was moistened with deionised water and ground in a domestic blender as described elsewhere [20]. Afterwards, PUF was filtered off in a vacuum system and squeezed between clean sheets of filter paper. PUF was then dried at 80°C for 1 h and stored in a dark bottle.

2.3 *Synthesis of Me-BTAO*

The Me-BTAO azo reagent was prepared as follows: 3.0 g of 6-methyl-2-aminobenzothiazole was weighted and stirred in 40.0 mL of hydrochloric acid at room temperature for 2 h. Deionised water (20.0 mL) was added slowly under mechanical stirring and the mixture was cooled to 0–5°C. Then 0.697 g of sodium nitrite in 20.0 mL of cold water was added dropwise to initiate the diazotisation reaction and the mixture was stirred for 2 h at 0–5°C. As a coupling reagent, 1,3-dihydroxy-5-methylbenzene (Orcinol) was utilised. To this end, 1.2 g of orcinol was dissolved in 20.0 mL of an 1.0 mol L^{-1} sodium carbonate solution and the mixture was cooled to 0–5°C. This solution was added dropwise to the above diazotised solution with vigorous stirring for 45 min. The mixture was kept overnight in a refrigerator at 0–5°C. Afterwards, the product was filtered and rinsed with cold water. The dark-red precipitate obtained was purified by recrystallisation with ethanol and active carbon. The solubility of the reagent Me-BTAO in various solvents was determined. It was found that the dye is insoluble in water and a 10% (v/v) hydrochloric acid solution. Me-BTAO is soluble in chloroform, acetone, ethanol, isopropanol and 5% (w/v) NaOH solution.

The infrared spectrum of the reagent in tablets of KBr was also obtained. An absorption peak is observed at 3400–3200 cm^{-1}. This peak indicates the presence of −OH functional group of alcohols or phenols, associated by hydrogen bond. This assignment can be confirmed by the presence of a −CO bond stretching at 1300–1200 cm^{-1}. The presence of a peak at 1060 cm^{-1} can be attributed to CN bond. Figure 2 show the proposed structure for Me-BTAO.

2.4 *Column preparation*

A 0.04% (w/v) Me-BTAO solution was percolated at a flow rate of 2.0 mL min^{-1} for 10 min through a laboratory-made cylindrical microcolumn (4.50 cm long, 4.0 mm i.d.) containing about 100 mg of polyurethane foam. Afterwards, the column was washed with
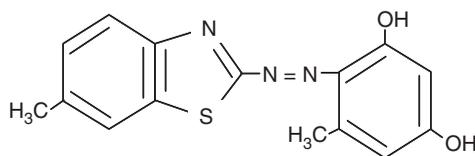
Figure 2. Molecular structure of 2-(6-methyl-2-benzothiazolylazo)-orcinol (Me-BTAO).

a 10% (w/v) sodium hydroxide solution to remove the excess of Me-BTAO until the red effluent became colourless. Then, the column was washed consecutively with 5% (v/v) nitric acid solution and deionised water at a flow rate of 1.5 mL min^{-1}. The rinsing step with nitric acid was mandatory in order to prevent PUF metal contamination.

The final amount of Me-BTAO impregnated on polyurethane foam was also determined. A flow of ethanol was passed through a minicolumn previously washed. The amount of the reagent Me-BTAO in a defined volume of effluent was determined spectrophotometrically. It was found that 0.20 mmol of the reagent Me-BTAO was loaded on each gram of the polyurethane foam.

Leaching of Me-BTAO from PUF with different solvents was studied. The tested solvent was percolated through a previously washed minicolumn at a flow rate of 1.50 mL/min for 30 min. The effluent from the column was analysed by molecular absorption spectrophotometry. Me-BTAO was not detected in the effluents, on using 1.0 mol L^{-1} hydrochloric or nitric acid solutions, TRIS buffer solution and deionised water.

2.5 *Collection and sample preparation*

Tap water samples were collected from Santo Amaro City, Bahia, Brazil, in several locations over the entire city. Samples were filtered through 0.45 μm pore membrane filters (cellulose acetate) immediately after collection, acidified to pH 2.0 with nitric acid and stored at 6°C in polyethylene bottles. The bottles were previously washed with a 10% (v/v) nitric acid solution and rinsed with ultrapure water.

2.6 *Analytical procedure*

The flow-based sorptive pre-concentration method initialises with the preconditioning of both sorbent columns (C2 and C1) with eluent (1.0 mol L^{-1} HCl) for 1 min and 50 s, respectively, whereupon V2 and V1 are consecutively switched to the load position with a delay time of 10 s. Thus, lead and cadmium are retained in both columns (C1 and C2) at a flow rate of 5.07 mL min^{-1} by sorptive chelation onto Me-BTAO loaded PUF (Figure 1a). After 10 mL sample loading, V2 is turned to the inject position (Figure 1b), whereby both metal ions in C2 are eluted and the eluate delivered to the FS-FAAS where selective detection of Cd takes place. Once the signal has been recorded, the FS-FAAS instrument is programmed to switch to the lead lamp, whereupon V1 is activated to the inject position to strip out the analytes from C1 with the subsequent recording of lead readout (Figure 1c). This operation is synchronised with the loading of the ensuing sample onto C2 (Figure 1c), thereby leading to improved analytical throughput. The analysis cycle lasted 80 s (45 samples per hour).

3. Results and discussion

3.1 *Optimisation of chemical and flow parameters for metal pre-concentration*

In order to optimise the analytical sorptive method a Box–Behnken design was performed selecting sample pH, buffer concentration (BC) and sampling flow rate (SR) as experimental variables. The coded and real values established in this model are compiled in Table 1. The model was evaluated for lead as being the FAAS sensitivity more than one order of magnitude lower than that of cadmium. All experiments were carried out in a

Table 1. Matrix design and experimental results of the Box–Behnken model for determination of lead at the $30\,g\,L^{-1}$.

Experiments	SR (mL min^{-1})	BC (mol L^{-1})	pH	Absorbance (AU)
1	3.0 (−1)	0.020 (−1)	8.5 (0)	0.0009
2	7.0 (1)	0.020 (−1)	8.5 (0)	0.0001
3	3.0 (−1)	0.050 (1)	8.5 (0)	0.0147
4	7.0 (1)	0.050 (1)	8.5 (0)	0.0158
5	3.0 (−1)	0.035 (0)	7.0 (−1)	0.0001
6	7.0 (1)	0.035 (0)	7.0 (−1)	0.0001
7	3.0 (−1)	0.035 (0)	10.0 (1)	0.0131
8	7.0 (1)	0.035 (0)	10.0 (1)	0.0189
9	5.0 (0)	0.020 (−1)	7.0 (−1)	0.0001
10	5.0 (0)	0.050 (1)	7.0 (−1)	0.0001
11	5.0 (0)	0.020 (−1)	10.0 (1)	0.0001
12	5.0 (0)	0.050 (1)	10.0 (1)	0.0193
13 (CP)	5.0 (0)	0.035 (0)	8.5 (0)	0.0372
14 (CP)	5.0 (0)	0.035 (0)	8.5 (0)	0.0311
15 (CP)	5.0 (0)	0.035 (0)	8.5 (0)	0.0301

Note: CP: central point.

random order using a standard solution of $30.0\,\mu g\,L^{-1}$ of Pb(II) and absorbance as the analytical response.

The model that better describes the variation of the absorbance (A) of Pb with the factors: pH, BC and SR using coded values is: $A = 0.0069 + 0.00075(SR) + 0.0061(BC) + 0.00637(pH) + 0.0054(SR)^2 + 0.0070(BC)^2 + 0.007(pH)^2 + 0.0005(SR)(BC) + 0.00145\ (SR)(pH) + 0.0048(BC)(pH)$. From this equation it is fairly easy to calculate the critical points for the entire set of variables investigated. Thus, in coded values the critical points are SR: 0.034, BC: 0.217 and pH: 0.230, which correspond to SR: $5.07\,mL\,min^{-1}$, BC: $0.038\,mol\,L^{-1}$ and pH: 8.85, respectively. These experimental conditions were also tested for cadmium pre-concentration using a sample volume of 10.0 mL of $10\,\mu g\,L^{-1}$ of Cd(II). The analytical signals were $> 0.146\,A.U$, evidencing that the optimum variables for Pb are also favorable for the uptake of cadmium by Me-BTAO loaded PUF under flow regime.

3.2 *Robustness test*

The robustness of an analytical method is defined as the measure of its capacity to reproduce results when the procedure is performed under slight changes in the nominal values established in the optimisation step [15]. In our case, the robustness test was performed by changing the optimised buffer concentration ($0.038\,mol\,L^{-1}$) and sampling flow rate ($5.07\,mL\,min^{-1}$) within ±5% and the optimum pH (8.85, adjusted with TRIS buffer) within ± 0.30 units of pH. Two 2^3 full factorial designs were performed by pre-concentrating 10.0 mL of sample at the $10.0\,\mu g\,L^{-1}$ level for Cd(II) and $30.0\,\mu g\,L^{-1}$ level for Pb(II). The results of these experiments are shown in Table 2. The evaluation of the factorial designs as Pareto charts (as can be seen in Figures 3 and 4) demonstrated that this pre-concentration system is robust for the factors studied within the range of BC: $0.038 \pm 0.002\,mol\,L^{-1}$, SR: $5.07 \pm 0.25\,mL\,min^{-1}$, and pH of 8.85 ± 0.30.

Table 2. Factorial design for evaluation of system robustness for cadmium and lead.

Experiments	pH	BC (mol L^{-1})	SR (mL min^{-1})	Absorbance Cd	Absorbance Pb
1	8.55 (−1)	0.036 (−1)	4.82 (−1)	0.1472	0.0341
2	9.15 (1)	0.036 (−1)	4.82 (−1)	0.1262	0.0432
3	8.55 (−1)	0.040 (1)	4.82 (−1)	0.1439	0.0332
4	9.15 (1)	0.040 (1)	4.82 (−1)	0.1294	0.0378
5	8.55 (−1)	0.036 (−1)	5.32 (1)	0.1468	0.0351
6	9.15 (1)	0.036 (−1)	5.32 (1)	0.1169	0.0389
7	8.55 (−1)	0.040 (1)	5.32 (1)	0.1490	0.0341
8	9.15 (1)	0.040 (1)	5.32 (1)	0.1120	0.0362
9	8.85 (0)	0.038 (0)	5.07 (0)	0.1395	0.0399
10	8.85 (0)	0.038 (0)	5.07 (0)	0.1401	0.0372
11	8.85 (0)	0.038 (0)	5.07 (0)	0.1375	0.0403
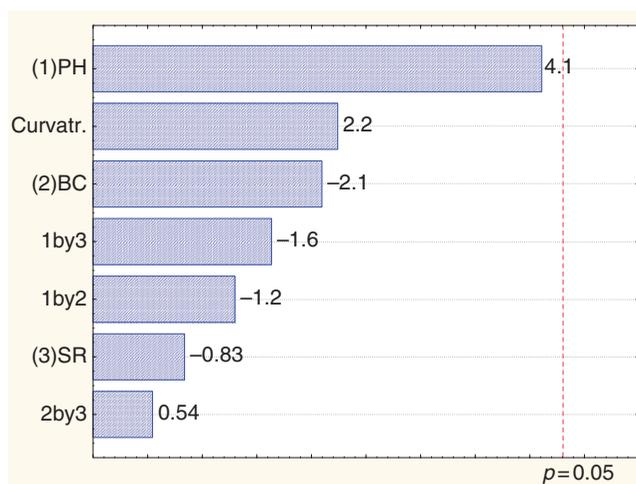
Figure 3. Pareto chart of robustness test for Cd.

3.3 *Validation studies*

The analytical performance of the proposed flow-through sorptive method was evaluated under the optimised values obtained with the Box–Benkhen model. Regression graphs were obtained by both direct sample aspiration into the nebuliser of FS-FAAS (conventional curve) and by flow injection pre-concentration exploiting the devised set-up. The pre-concentration factors, calculated as the ratio between the sensitivity of the proposed pre-concentration method and that of the conventional aspiration procedure, were 38.6 and 30.0 for Cd and Pb, respectively.

The detection limits (LOD) calculated following the IUPAC recommendations [21] were $0.08\,\mu g\,L^{-1}$ and $0.51\,\mu g\,L^{-1}$, for cadmium and lead, respectively, and the quantification limits (LOQ) were 0.27 and $1.72\,\mu g\,L^{-1}$, respectively.

The repeatability of the method expressed as the relative standard deviation (RSD) of seven consecutive replicates was 1.63 and 3.87% for cadmium at the $2.0\,\mu g\,L^{-1}$ and
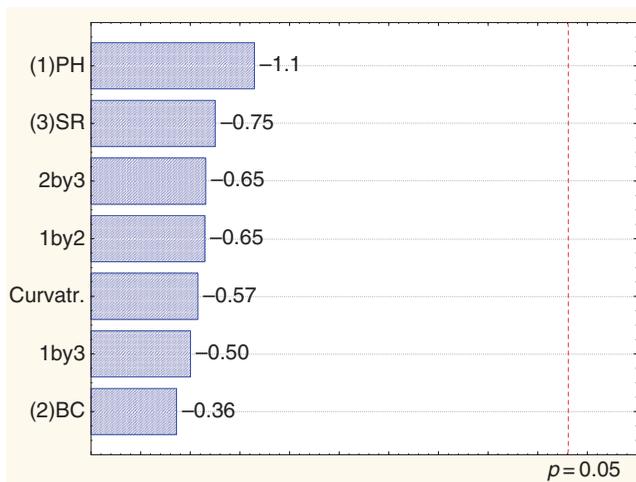
Figure 4. Pareto chart of robustness test for Pb.

Table 3. Application of the proposed flow-based sorptive pre-concentration method to the determination of lead and cadmium in drinking waters.

Sample	Cd (μg L^{-1}) Found	Pb (μg L^{-1}) Found
1	0.91 ± 0.10	4.64 ± 0.31
2	0.68 ± 0.05	3.67 ± 0.50
3	0.51 ± 0.02	2.49 ± 0.20
4	0.47 ± 0.01	6.24 ± 0.40
5	0.52 ± 0.04	3.67 ± 0.50
6	0.38 ± 0.06	4.64 ± 0.31
7	0.35 ± 0.02	4.09 ± 0.90
8	0.34 ± 0.04	2.49 ± 0.20
9	0.51 ± 0.02	5.82 ± 0.87
10	0.66 ± 0.18	5.68 ± 1.01
11	0.91 ± 0.11	2.29 ± 0.35
12	0.38 ± 0.06	4.44 ± 0.64

Note: Results are given as mean $\pm$ standard deviation ($n = 3$).

$10.0\,\mu$g L^{-1} levels, respectively, and 6.34% and 3.26% for lead at the $5.0\,\mu$g L^{-1} and $30.0\,\mu$g L^{-1} levels, respectively.

The calibration equations obtained using the flow-based pre-concentration procedure were A = 0.0116[Cd, μg L^{-1}] + 0.0037, $R^2 = 0.9987$ for cadmium and A = 0.0009[Pb, μg L^{-1}] + 0.0058, $R^2 = 0.9989$ for lead. The number of standard samples and the replicates were 7 and 3, respectively. The on-line pre-concentration system proposed features a dynamic linear range from 0.27 to $80.0\,\mu$g L^{-1} and from 1.72 to $50.0\,\mu$g L^{-1} for Cd and Pb, respectively.

The calibration linearity was evaluated considering two parameters: the so-called on-line linearity (LIN$_{OL}$) and the in-line linearity (LIN$_{in}$) [15]. The LIN$_{OL}$ is defined as the

degree of dispersion of the data utilised for building the calibration curve. It is calculated by the expression $100[1-RSD(b)]$, where RSD(b) is the relative standard deviation of the slope. For the calibration curve of Cd the RSD(b) was 0.011 and thus the LIN_{OL} was 98.8%. For the calibration curve of Pb LIN_{OL} was 99.1%. The LIN_{IN} refers to the linear adjustment of the values of the analytical signals obtained experimentally in relation to the concentration of the analyte, that is, goodness-of-fit, which is checked by the lack-of-fit test. This parameter is evaluated by the p-value. A p-value lower than 5% shows lack-of-fit in the data of the analytical curve [22,23]. According to data in the calibration plot of Cd, the p-value was 9.73. On the other hand, the calibration plot reveals that p-value was 6%.

The consumptive index (CI, defined as the sample volume, in mL, consumed in order to achieve a unit of enrichment factor, (EF)) [24] was calculated as $CI = V_s/EF$, where V_s is the sample volume, in this case 10.0 mL for both Pb and Cd. For cadmium CI was 0.26 mL and for lead amounted to 0.33 mL. The analytical throughput expressed as the number of samples injected per hour was $45\,h^{-1}$. The concentration efficiency defined as the enrichment factors obtained by the flow system in one minute were 19.3 and 15 for Cd and Pb, respectively.

The sorption capacity of the loaded sorbent for the retention of cadmium and lead was also determined. The following general procedure was carried out: about 100 mg of the solid sorbent was equilibrated with 100 mL of $10.0\,\mu g\,mL^{-1}$ Cd and Pb solutions at pH 8.85 for 4 h in separate flasks under vigorous stirring. The systems were filtered by gravity and metals were determined in each filtrate by FAAS. The maximum retention capacity of the Me-BTAO loaded microcolumn was 4.64 and $2.60\,\mu mol\,g^{-1}$ for Cd and Pb, respectively.

In order to assess the trueness of the procedure cadmium and lead were determined in the certified reference material SRM 1643d (Trace elements in natural water) supplied by the US National Institute of Standards & Technology. The certified values are $6.47 \pm 0.37\,\mu g\,L^{-1}$ and $18.15 \pm 0.64\,\mu g\,L^{-1}$ for Cd and Pb, respectively. The results found with the optimised pre-concentration system were $6.05 \pm 0.27\,\mu g\,L^{-1}$ and $17.85 \pm 0.71\,\mu g\,L^{-1}$, for Cd and Pb, respectively. The application of the t-test of comparison of the experimental means and certified concentrations demonstrated the inexistence of significant differences at the 95% confidence level. The CRM has other metal ions with typical concentrations for natural water samples.

The interfering effect of other metal ions potentially found in natural waters on the sorptive pre-concentration method was studied using 10 mL of a solution containing cadmium $(10\,\mu g\,L^{-1})$ and lead $(30\,\mu g\,L^{-1})$ in the presence of nickel, chromium cobalt, zinc, aluminum, iron, manganese, mercury, molybdenum and vanadium, all at a concentration level of $100\,\mu g\,L^{-1}$. Experimental results revealed that no interferences at the 5% level were encountered for any of the assayed metal species at a $100\,\mu g\,L^{-1}$ level. It was also found that cadmium and lead do not interfere in the determination of each other when present at concentrations of $100\,\mu g\,L^{-1}$.

3.3 *Analysis of real samples*

The proposed method was applied to the determination of cadmium and lead in tap water samples collected in Santo Amaro City, Bahia, Brazil, and processed as detailed under Experimental. Twelve samples were analysed and the concentrations of cadmium and lead found varied from 0.34 to $0.91\,\mu g\,L^{-1}$ and 2.3 to $6.2\,\mu g\,L^{-1}$, respectively.

The concentrations of lead and cadmium encountered in the collected samples were in all instances lower than the maximum allowed levels endorsed by Brazilian regulations [25], which are 5 and $10 \mu g L^{-1}$ for cadmium and lead, respectively (Table 3).

4. Conclusions

In this work, an on-line simultaneous pre-concentration procedure was devised and applied to the determination of Cd and Pb by sequential multi-element FAAS. The proposed procedure is proven to be accurate, fast and precise for quantitative determination of Cd and Pb in drinking waters. Moreover, the Me-BTAO reagent immobilised onto PUF is very stable for both target metal species. The limit of quantification of the optimised method allowed the determination of cadmium and lead in natural waters below the levels endorsed by Brazilian regulatory authorities.

Acknowledgements

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