

Development of a method for the determination of cadmium levels in seawater by flame atomic absorption spectrometry using an online cloud-point extraction system

Rafael Vasconcelos OLIVEIRA^{1,2}, Uelber Silva VIEIRA³, Mardson Vasconcelos MACIEL³,
Thais Souza NERI³, Grazielle Santos SALES³, Rebeca Moraes MENEZES¹,
Valfredo Azevedo LEMOS^{1,3,*}

¹Graduate Program in Chemistry, Federal University of Bahia, Salvador, Bahia, Brazil

²Bahia Federal Institute of Education, Science and Technology, Irecê, Bahia, Brazil

³Laboratory of Analytical Chemistry, State University of Southwestern Bahia, Jequié, Bahia, Brazil

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Abstract: A new system was developed for the preconcentration and determination of cadmium levels in water following online cloud-point extraction and analysis by flame atomic absorption spectrometry. The method uses cloud-point extraction of the complex formed between Cd(II) ions and the reagent 2-(5-bromo-2'-thiazolylazo)-*p*-cresol (Br-TAC) using Triton X-114 as a surfactant. The main steps of the procedure, extraction, filtration, and detection were conducted online. Parameters that influence the experimental conditions of online preconcentration systems were examined, including pH, concentration of reagent and surfactant, and flow of sample and eluent. The limit of detection of the method is $0.2 \mu\text{g L}^{-1}$. The preconcentration system exhibits an enrichment factor of 19, an analytical frequency of 60 h^{-1} , and a consumptive index of 0.12 mL. The procedure was applied to the determination of cadmium levels in seawater samples.

Key words: Cadmium, online preconcentration, cloud-point extraction, seawater

1. Introduction

Cadmium, a trace element that accumulates in vital human organs, is toxic even at low concentrations. The main cadmium absorption routes for humans are food, water, and exposure to cigarette smoke¹ The absorption of this element can cause serious harmful effects in humans, such as the development of mental retardation and attention difficulties, as well as adverse effects on the cardiovascular system and on blood composition, especially in children² Water is one of the main routes of cadmium contamination in humans. Nonpolluted seawater has very low levels of the element. However, human activities have introduced cadmium in seawater at quantities higher than natural. The cadmium content in seawater provides an indication of the level of contamination of the area. Thus, the dosage of cadmium in this matrix is crucial³

Several spectrometric detection techniques are employed for the determination of cadmium levels. Among these techniques, molecular absorption spectrophotometry, atomic absorption spectrometry, and inductively coupled plasma-mass spectrometry are most commonly used⁴⁻⁷ However, analyte levels are often below the limit of detection for most of these techniques. Therefore, a pretreatment is needed to increase the sensitivity of the detection technique.

*Correspondence: vlemos@uesb.edu.br

In recent years, methods have been developed for preconcentration and determination of trace species using several matrices. These methods are mainly based on coprecipitation, liquid-liquid extraction, solid-phase extraction, and cloud-point extraction^{8–14} Compared to other techniques, cloud-point extraction offers many advantages, including high frequency rates, simplicity, high enrichment factors, easy automation, low cost, and reduced use of reagents. Cloud-point extraction has been widely used in the extraction and preconcentration of metals, organic species, biomolecules, and chelates¹⁵ The extraction is based on separation of the analyte from the matrix with the aid of micelles formed by a surfactant reagent. The combination of micelles and analyte is called the rich phase. The target analyte is finally measured in the rich phase¹⁶

The combination of cloud-point extraction with online systems provides a promising tool for the analysis of toxic metals due to high sensitivity and reproducibility, efficient removal of interfering compounds, high extraction efficiency, and low amounts of reagents and samples required. In addition, the centrifugation step commonly used in cloud-point extraction is avoided, making the process simpler and the analysis faster.^{17–20}

In this work, we developed a method for the determination of cadmium levels in water samples using an online preconcentration system with cloud-point extraction and detection by flame atomic absorption spectrometry.

2. Results and discussion

2.1. Optimization of extraction parameters

The optimization of experimental conditions was performed using the univariate method. A $5.0 \mu\text{g L}^{-1}$ cadmium solution was used in the optimization experiments.

2.1.1. pH

The effect of pH on the determination of cadmium levels using cloud-point extraction was evaluated. It has been reported that similar compounds to the Br-TAC form complexes with cadmium at pH 4–9.²¹ Cadmium solutions were prepared at different pH values and subjected to the preconcentration process. Figure 1 demonstrates that the formation of the extracted Cd (II)/Br-TAC complex is strongly influenced by pH, and the pH range that yielded the best results is between 7.0 and 8.0. After pH 8.0, a decrease occurs in the analytical signal, probably due to the formation of Cd complexes with hydroxide ions. Therefore, in subsequent experiments, a pH 7.7 borate buffer solution was used for pH control.

2.1.2. Concentration of eluent

Since the sorption of cadmium is strongly influenced by pH, substances that induce a rapid change in pH may be suitable eluents for this system. Hydrochloric acid solutions of varying concentration, 0.00 to 0.50 mol L^{-1} , were tested as eluents. The results show that desorption of the analyte is most pronounced at concentrations higher than 0.075 mol L^{-1} (Figure 2). The concentration of HCl in the eluent was 0.10 mol L^{-1} for all subsequent experiments.

2.1.3. Amount of filtering material

A study on the influence of the mass of filter material in the preconcentration system was also performed. The amount of material in the minicolumn must be sufficient for proper extraction of the micelles. The type of material (polyester) was selected according to previous experiments¹⁷ The experiments were performed with polyester masses ranging from 100 to 250 mg. After construction of the minicolumns, polyester filling was

washed with alcohol, 2.0 mol L^{-1} nitric acid, and ultrapure water, in that order. Each minicolumn was then used in the preconcentration system for the cloud-point extraction and determination of cadmium levels. The best results were obtained when 150 mg of material was used (Figure 3). Above this value, the signal decreased. Additionally, too much polyester in the minicolumn resulted in backpressure in the system, causing leaks.

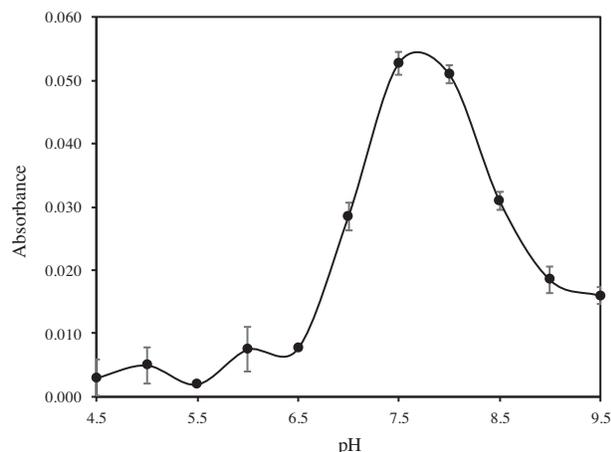


Figure 1. Influence of pH on the preconcentration of cadmium. Other experimental conditions: concentration of eluent, 0.20 mol L^{-1} ; reaction mixture flow rate, 5.00 mL min^{-1} ; eluent flow rate, 6.0 mL min^{-1} ; amount of filtering material, 100 mg; concentration of surfactant, $2.5 \times 10^{-2}\%$ (w/v); concentration of chelating reagent, $3.0 \times 10^{-8} \text{ mol L}^{-1}$.

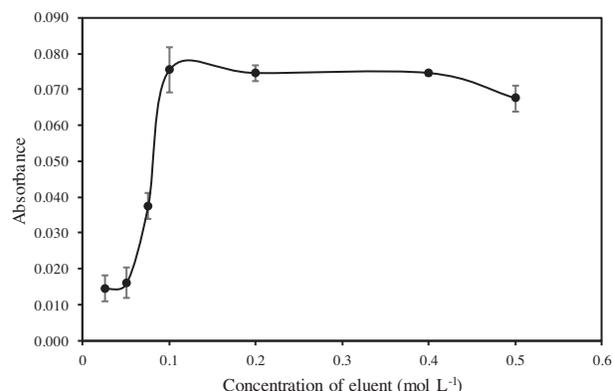


Figure 2. Influence of eluent concentration on the preconcentration of cadmium. Other experimental conditions: pH, 7.7; reaction mixture flow rate, 5.00 mL min^{-1} ; eluent flow rate, 6.0 mL min^{-1} ; amount of filtering material, 100 mg; concentration of surfactant, $2.5 \times 10^{-2}\%$ (w/v); concentration of chelating reagent, $3.0 \times 10^{-8} \text{ mol L}^{-1}$.

2.1.4. Concentration of surfactant and chelating reagent

The extraction of Cd(II) is based on the formation of a complex with Br-TAC. Thus, a suitable Cd(II)/Br-TAC ratio had to be ascertained. Experiments were performed using Br-TAC solutions with final concentrations ranging from 1.3×10^{-8} to $2.7 \times 10^{-7} \text{ mol L}^{-1}$. The concentration of Triton X-114 was fixed at $2.5 \times 10^{-2}\%$ (w/v). The graph in Figure 4 suggests that the best results are obtained when a $6.5 \times 10^{-8} \text{ mol L}^{-1}$ Br-TAC solution is used. Above this value, additional reagent causes a decrease in absorbance. A $6.5 \times 10^{-8} \text{ mol L}^{-1}$ Br-TAC solution was used in subsequent experiments. The influence of surfactant concentration on the extraction was also studied by varying the concentration of Triton X-114 between 1.0×10^{-3} and $2.5 \times 10^{-2}\%$ (w/v). These experiments were performed with a Br-TAC concentration of $4.50 \times 10^{-7} \text{ mol L}^{-1}$. The best results were obtained when Triton X-114 concentrations were maintained between 1.0×10^{-2} and $2.5 \times 10^{-2}\%$ (w/v). In later experiments, a $1.5 \times 10^{-2}\%$ (w/v) Triton X-114 solution was used.

2.1.5. Reaction mixture flow rate

The rotation of the peristaltic pump P1 controls the flow of aspiration of the sample and the surfactant/Br-TAC mixture. Furthermore, the pump controls the flow rate of the reaction mixture through the reaction coil and the minicolumn. The influence of the reaction mixture flow rate in the preconcentration system was studied. According to the results shown in Figure 5, flow rates in the range of 6.80 to 9.10 mL min^{-1} resulted in the highest analytical signals. In all subsequent experiments, a flow rate of 7.00 mL min^{-1} was employed.

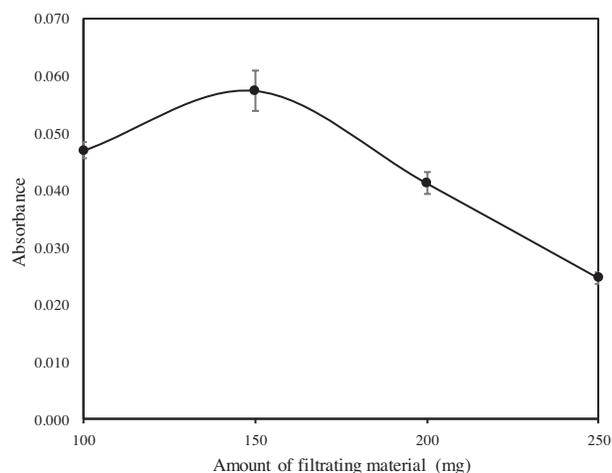


Figure 3. Influence of filtrating material amount on the preconcentration of cadmium. Other experimental conditions: pH, 7.7; reaction mixture flow rate, 5.00 mL min^{-1} ; concentration of eluent, 0.10 mol L^{-1} ; eluent flow rate, 6.0 mL min^{-1} ; concentration of surfactant, $2.5 \times 10^{-2} \%$ (w/v); concentration of chelating reagent, $3.0 \times 10^{-8} \text{ mol L}^{-1}$.

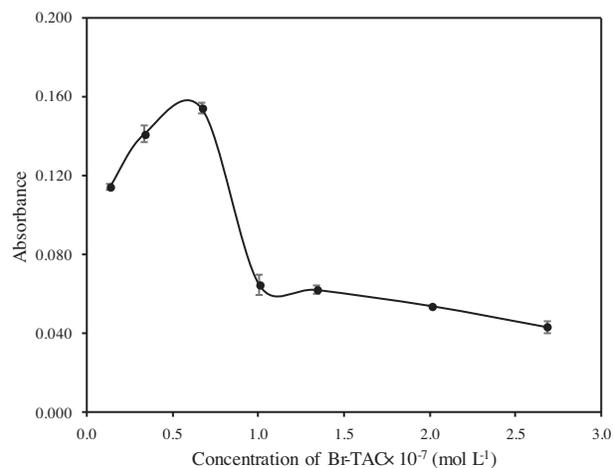


Figure 4. Influence of the amount of Br-TAC on the preconcentration of cadmium. Other experimental conditions: pH, 7.7; reaction mixture flow rate, 5.00 mL min^{-1} ; concentration of eluent, 0.10 mol L^{-1} ; amount of filtrating material, 150 mg; eluent flow rate, 6.0 mL min^{-1} ; concentration of surfactant, $2.5 \times 10^{-2} \%$ (w/v).

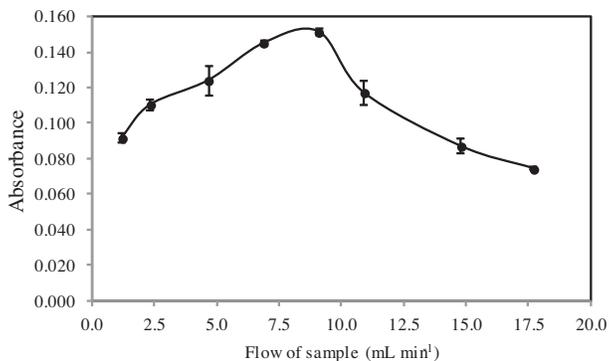


Figure 5. Influence of the sample flow rate on the preconcentration of cadmium. Other experimental conditions: pH, 7.7; reaction mixture flow rate, 5.00 mL min^{-1} ; concentration of eluent, 0.10 mol L^{-1} ; amount of filtrating material, 150 mg; eluent flow rate, 6.0 mL min^{-1} ; concentration of surfactant, $1.5 \times 10^{-2} \%$ (w/v); concentration of chelating reagent, $6.5 \times 10^{-8} \text{ mol L}^{-1}$.

2.1.6. Eluent flow rate

The effect of the eluent flow rate (2.4 to 9.6 mL min^{-1}) in the online preconcentration system with cloud-point extraction was studied. The study of this parameter is important because very high flow rates may be incompatible with the flow of the nebulizer. On the other hand, if the eluent flow rate is too low, desorption occurs very slowly, causing flares in the transient signal and decreasing absorbance. The best results were obtained using eluent flow rates between 5.0 and 7.7 mL min^{-1} . In subsequent experiments, a value of 6.0 mL min^{-1} was used.

2.2. Selectivity

The influence of some potential interfering ions on the proposed system was also investigated. Solutions of cadmium ($10.0 \mu\text{g L}^{-1}$) were prepared and amounts of each species were added. The proposed procedure was applied and the analytical signal was compared with the analytical signal corresponding to the solution containing only cadmium. The following ions do not interfere in the system when present in the amounts indicated in parentheses: Mn^{2+} , Pb^{2+} , and Zn^{2+} ($100 \mu\text{g L}^{-1}$); Cu^{2+} and Fe^{3+} ($50 \mu\text{g L}^{-1}$); Ni^{2+} ($20 \mu\text{g L}^{-1}$).

2.3. Analytical features

After the optimization of the preconcentration conditions, the analytical characteristics of the method were calculated. A calibration curve for the preconcentration system was obtained by employing solutions of Cd(II) at concentrations ranging between 1.0 and $10.0 \mu\text{g L}^{-1}$. The corresponding equation is $A = 1.55 \times 10^{-2}C + 2.60 \times 10^{-3}$, where A is the analytical signal and C is the concentration of cadmium ($\mu\text{g L}^{-1}$). The corresponding analytical curve for the direct measurement of cadmium levels in the spectrometer was also calculated for comparison; the resulting equation is $A = 8.16 \times 10^{-4}C + 5.70 \times 10^{-3}$. The detection limit and precision of the method were $0.2 \mu\text{g L}^{-1}$ and 5.4%, respectively. Blank signals ranged from 0.000 to 0.0002. The enrichment factor (EF) was calculated from the ratio between the slopes of the linear sections of the analytical curves obtained with the proposed system and the direct measurement on the FAAS, respectively²². The enrichment factor obtained for this method is 19. Other characteristic parameters of the preconcentration systems were also evaluated, including the consumptive index (0.12 mL), concentration efficiency (19 min^{-1}), and analytical frequency (60 h^{-1}). The parameters were calculated following methods previously described in the literature²².

2.4. Application

The proposed procedure was applied to the determination of cadmium levels in natural water samples. The results are shown in Table 1. Recovery (R) was calculated as $R = \frac{C-C_0}{m} \bullet 100$, where C and C_0 are the cadmium levels found in the samples with and without addition, respectively, and m is cadmium content added. Recovery values of 96% and 108% indicate that the procedure was successful in determining the cadmium levels. The samples were also subjected to the determination of cadmium employing ET AAS. There were no significant differences between the results.

Table 1. The results for the determination of cadmium levels in seawater samples using the proposed procedure. The uncertainties are presented at the 95% confidence level (n = 4).

Sample	Amount of cadmium ($\mu\text{g L}^{-1}$)			Recovery (%)
	Added	Found		
		Proposed method	ET AAS	
Seawater 1	0.0	<LOD	—	108
	5.0	5.4 ± 0.2	5.1 ± 0.5	
Seawater 2	0.0	<LOD	—	96
	5.0	4.8 ± 0.5	5.2 ± 0.1	

3. Experimental

3.1. Apparatus

A PerkinElmer flame atomic absorption spectrometer (AAnalyst 200, Shelton, CT, USA) equipped with a deuterium lamp for background correction was used for absorbance measurements. A hollow cathode lamp (Cd) was used as a radiation source operating at 228.80 nm wavelength. The flow rates of acetylene and air were 2.5 L min^{-1} and 10.0 L min^{-1} , respectively. The aspiration flow rate of the nebulizer was 6.0 mL min^{-1} . An atomic absorption spectrometer (PerkinElmer, model AAnalyst 400) equipped with a graphite furnace (PerkinElmer, Model HGA 900) was used for results by electrothermal atomic absorption spectrometry (ET AAS).

The online system using cloud-point extraction consisted of five three-way direct-lift solenoid valves (Cole-Parmer, Vernon Hills, IL, USA), two peristaltic pumps of four channels (Milan model 204, Colombo, Brazil), and silicone and Teflon tubing. A Digimed (model DM 20, Santo Amaro, Brazil) pH meter was used for pH measurements. The minicolumn was constructed from a polyvinyl chloride tube ($3.50 \text{ cm} \times 0.40 \text{ cm}$) and packed with polyester. A schematic representation of the online preconcentration system is shown in Figure 6.

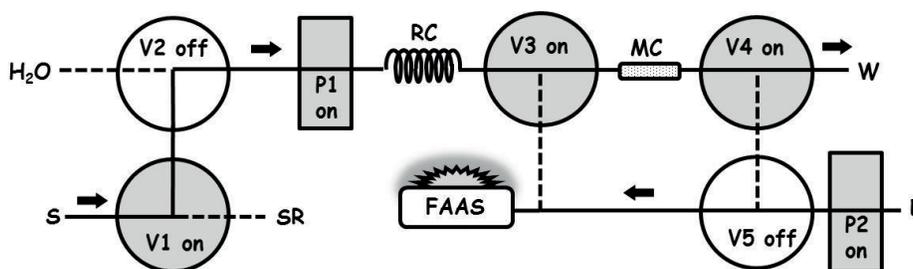


Figure 6. Schematic representation of the online preconcentration system for determination of cadmium. V1, V2, V3, V4, and V5: solenoid valves; P1 and P2: peristaltic pumps; RC: reaction coil; MC: minicolumn; FAAS: flame atomic absorption spectrometer; S: sample; SR: mixture of surfactant and reagent; E: eluent; W: waste. Step: 1 (see Table 2).

3.2. Reagents

Ultrapure doubly distilled water from a water purification system (Elga, Purelab Classic model, High Wycombe, Bucks, UK) was used to prepare all solutions. All glassware was maintained for 24 h in a 5.0% (v/v) nitric acid solution. All reagents used were of analytical grade. Working solutions at $\mu\text{g L}^{-1}$ levels were prepared daily by dilution of a $1000 \mu\text{g mL}^{-1}$ Cd stock solution (Merck). Br-TAC solutions were prepared by dissolving appropriate amounts of the laboratory-synthesized solid in absolute ethanol (Merck, Darmstadt, Germany). Triton X-114 solutions were prepared by dissolving an appropriate volume of commercially available surfactant (Sigma-Aldrich, Milwaukee, WI, USA) in water. The pH of solutions for extraction was adjusted using buffer solutions: acetate for pH 4.7–5.5, phosphate for pH 6.0–6.5, borate for pH 7.0–8.0, and ammonia for pH 9.0–9.3.

3.3. Synthesis of Br-TAC

Synthesis of Br-TAC was performed according prior procedures.^{17,23} 2-Amino-5-bromothiazole (2.0 g) was dissolved in 50 mL of a 6.0 mol L^{-1} hydrochloric acid solution at $0\text{--}5 \text{ }^\circ\text{C}$. A solution containing 0.53 g of sodium nitrite in water (20 mL) was added dropwise with vigorous stirring over 45 min. In this step, the temperature was maintained at $0\text{--}5 \text{ }^\circ\text{C}$. A mixture containing 1.21 g of p-cresol in 20 mL of 1.0 mol L^{-1}

sodium carbonate solution was then added dropwise to the diazotate. This addition was performed at 0–5 °C under vigorous stirring. The reaction mixture was stored in a refrigerator at 0–5 °C for 12 h. The solid obtained was filtered and washed with cold water. The product was recrystallized with ethanol and activated charcoal.

3.4. Preconcentration system

The steps of a complete cycle for the preconcentration and determination of cadmium levels using the online preconcentration system with cloud-point extraction are shown in Table 2. In the first step, the sample was aspirated for 20.0 s at a flow rate of 7.0 mL min⁻¹. Then the surfactant/Br-TAC solution was aspirated for 5.0 s. The reaction mixture was propelled by the reaction coil following actuation of valve V3. In this step, a flow of water was also introduced into the system to carry the mixture and to wash the ducts. The fourth stage of the cycle was desorption of Cd(II) from the minicolumn by the eluent and subsequent analysis in the spectrometer. The analytical signal was measured as the maximum absorbance. The period of one complete cycle was 60 s.

Table 2. Operation of online preconcentration system for the determination of cadmium levels.

Step	Time (s)	Valve position					Peristaltic pump		Operation
		V1	V2	V3	V4	V5	P1	P2	
1	20	on	off	on	on	off	on	on	Sample aspiration
2	5	off	off	on	on	off	on	on	Reagent and surfactant mixture aspiration
3	15	off	on	on	on	off	on	on	Percolation of reaction mixture by minicolumn; carrying and washing
4	20	off	on	off	off	on	off	on	Elution of Cd(II) ions from minicolumn; reading

Table 3. Characteristics of methods for the preconcentration of cadmium. EF: enrichment factor; f: analytical frequency; LOD: limit of detection; RSD: relative standard deviation; CPE: cloud-point extraction; SPE: solid-phase extraction; FAAS: flame atomic absorption spectrometry; CVAAS: cold vapor atomic absorption spectrometry; ETAAS: electrothermal atomic absorption spectrometry.

Extraction technique	EF	f(h ⁻¹)	LOD ($\mu\text{g L}^{-1}$)	CE (h ⁻¹)	RSD (%)	Detection technique	Sample	Reference
SPE	20	28	2.1×10^{-3}	9	2.5	CV AAS	Water	24
SPE	105	22	0.1	38	3.3	FAAS	Water and urine	25
SPE	37	27	0.06	17	1.9–3.7	ETAAS	Urine	26
SPE	41	45	0.11	31	0.3	FAAS	Water	27
SPE	12	—	0.65	—	—	FAAS	Food and water	28
Precipitation	41	—	0.006	—	4.3	ETAAS	Water	29
CPE	157	—	0.33	—	3.0	FAAS	Water	30
CPE	—	—	0.27	—	2.5	FAAS	Water	31
CPE	29	—	0.1*	—	0.9	FAAS	Water	32
CPE	20	—	0.03	—	3.7	FAAS	Seawater and effluent	33
CPE	19	60	0.20	19	5.4	FAAS	Water	This work

*value in $\mu\text{g g}^{-1}$

4. Conclusion

The preconcentration system was optimized and successfully applied to the determination of cadmium levels in natural water samples. The incorporation of cloud-point extraction in an online preconcentration system afforded several advantages such as fast analyses, high enrichment factors, high analytical frequencies, and low waste production. Additionally, the system enables low consumption of sample and reagents and the elimination of centrifugation and cooling steps. Table 3 shows a comparison between the method developed and other procedures involving preconcentration of cadmium previously described in the literature. The proposed procedure has a low enrichment factor when compared to other methods. However, the online system provides a significantly high frequency rate. This large number of samples analyzed per hour also results in a high concentration efficiently. Thus, it can be observed that a major advantage of this method in relation to those in Table 3 is its speed. The analytical characteristics indicate that this method is a good alternative to the determination of cadmium levels in natural water samples.

Acknowledgments

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References

1. Moghimi, A.; Poursharifi, M. J. *Asian J. Chem.* **2011**, *23*, 1429-1434.
2. Farahani, M. D.; Shemirani, F. *Microchim. Acta* **2012**, *179*, 219-226.
3. Omanovic, D.; Kwokal, Z.; Goodwin, A.; Lawrence, A.; Banks, C. E.; Compton, R. G.; Komorsky-Lovric, S. *J. Iran. Chem. Soc.* **2006**, *3*, 128-139.
4. Sereshti, H.; Heravi, Y. E.; Samadi, S. *Talanta* **2012**, *97*, 235-241.
5. Xiang, G. Q.; Wen, S. P.; Wu, X. Y.; Jiang, X. M.; He, L. J.; Liu, Y. L. *Food Chem.* **2012**, *132*, 532-536.
6. Meeravali, N. N.; Kumar, S. J. *Anal. Methods-UK*, **2012**, *4*, 2435-2440.
7. Bayrak, H. E.; Bulut, V. N.; Tufekci, M.; Bayrak, H.; Duran, C.; Soylyak, M. *Turk. J. Chem.* **2016**, *40*, 93-105.
8. Li, Y. J.; Hu, B. *Atom. Spectrosc.* **2009**, *30*, 104-111.
9. Gil, R. A.; Salonia, J. A.; Gasquez, J. A.; Olivieri, A. C.; Olsina, R.; Martinez, L. D. *Microchem. J.* **2010**, *95*, 306-310.
10. Baliza, P. X.; Teixeira, L. S. G.; Lemos, V. A. *Microchem. J.* **2009**, *93*, 220-224.
11. Bazmandegan-Shamili, A.; Haji Shabani, A. M.; Dadfarnia, S.; Saeidi, M.; Rohani Moghadam, M. *Turk. J. Chem.* **2015**, *39*, 1059-1068.
12. Novaes, C. G.; Santos, J. S.; Ferreira, S. L. C.; Lemos, V. A. *J. AOAC Int.* **93**, 1609-1615.
13. Dmitrienko, S. G.; Sviridova, O. A.; Pyatkova, L. N.; Senyavin, V. M. *Anal. Bioanal. Chem.* **2002**, *374*, 361-368.
14. Tuzen, M.; Citak, D.; Soylyak, M. *J. Hazard. Mater.* **2008**, *158*, 137-141.
15. Aranda, P. R.; Gil, R. A.; Moyano, S.; De Vito, I.; Martinez, L. D. *Talanta* **2008**, *77*, 663-666.
16. Giokas, D. L.; Paleologos, E. K.; Karayannis, M. I. *Anal. Bioanal. Chem.* **2002**, *373*, 237-243.
17. Lemos, V. A.; Baliza, P. X.; de Carvalho, A. L.; Oliveira, R. V.; Teixeira, L. S. G.; Bezerra, M. A. *Talanta* **2008**, *77*, 388-393.
18. Ortega, C.; Gomez, M. R.; Olsina, R. A.; Silva, M. F.; Martinez, L. D. *J. Anal. At. Spectrom.* **2002**, *17*, 530-533.
19. Garrido, M.; Di Nezio, M. S.; Lista, A. G.; Palomeque, M.; Band, B. S. F. *Anal. Chim. Acta* **2004**, *502*, 173-177.

20. Fang, Q.; Du, M.; Huie, C. W. *Anal. Chem.* **2001**, *73*, 3502-3505.
21. Lemos, V. A.; Santos, E. S.; Santos, M. S.; Yamaki, R. T. *Microchim. Acta* **2007**, *158*, 189-204.
22. Fang, Z. L.; Dong, L. P.; Xu, S. K. *J. Anal. At. Spectrom.* **1992**, *7*, 293-299.
23. Yamaki, R. T.; Nunes, L. S.; de Oliveira, H. R.; Araujo, A. S.; Bezerra, M. A.; Lemos, V. A. *J. AOAC Int.* **2011**, *94*, 1304-1309.
24. Sahan, S.; Sahin, U. *Talanta* **2012**, *88*, 701-706.
25. Giakissikli, G.; Zachariadis, P.; Kila, I.; Teshima, N.; Anthemidis, A. *Anal. Lett.* **2016**, *49*, 929-942.
26. Giakissikli, G.; Quezada, A. A.; Tanaka, J.; Anthemidis, A. N.; Murakami, H.; Teshima, N.; Sakai, T. *Anal. Sci.* **2015**, *31*, 383-389.
27. Zhao, S. L.; Chen, F. S.; Zhang, J.; Ren, S. B.; Liang, H. D.; Li, S. S. *J. Ind. Engin. Chem.* **2015**, *27*, 362-367.
28. Sivrikaya, S.; Imamoglu, M.; Yildiz, S. Z.; Kara, D. *Anal. Lett.* **2016**, *49*, 943-957.
29. Wen, X. D.; Yang, S. C.; Zhang, H. Z.; Deng, Q. W. *Microchem. J.* **2016**, *124*, 60-64.
30. Arvand, M.; Pourhabib, A.; Afshari, A.; Bagherinia, M.; Ghodsi, N.; Shemshadi, R. *J. Anal. Chem.* **2008**, *63*, 954-959.
31. Naeemullah; Kazi, T. G.; Tuzen, M. *J. Ind. Engin. Chem.* **2016**, *35*, 93-98.
32. Moghimi, A.; Tajodini, N. *Asian J. Chem.* **2010**, *22*, 5025-5033.
33. Escalera, L. A.; Santelli, R. E.; Oliveira, E. P.; de Carvalho, M. F. B.; Bezerra, M. A. *Int. J. Environ. Anal. Chem.* **2009**, *89*, 515-527.