



# On-line preconcentration system using a minicolumn of polyurethane foam loaded with Me-BTABr for zinc determination by Flame Atomic Absorption Spectrometry

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## Abstract

In the present paper, an on-line system for preconcentration and determination of zinc by Flame Atomic Absorption Spectrometry (FAAS) is proposed. It is based in the sorption of zinc(II) ions on a minicolumn packed with polyurethane foam loaded with 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTABr) reagent. Chemical and flow variables as pH effect, sample flow rate and eluent concentration were optimized using univariate methodology. The results demonstrated that zinc can be determined using the sample pH in the range of 6.5–9.2, sample flow rate of 6.0 ml min<sup>-1</sup>, and the elution step using 0.10 mol l<sup>-1</sup> hydrochloric acid solution at flow rate of 5.5 ml min<sup>-1</sup>. In these conditions, an enrichment factor of 23 and a sampling rate of 48 samples per hour were achieved. The detection limit (DL, 3σ) as IUPAC recommendation was 0.37 μg l<sup>-1</sup> and the precision (assessed as the relative standard deviation, R.S.D.) reached values of 5.9–1.8% in zinc solutions of 1.0–10.0 μg l<sup>-1</sup> concentration, respectively. The method was successfully applied to the determination of trace amounts of zinc in natural water samples from Salvador (Brazil).

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**Keywords:** Preconcentration; Me-BTABr; Zinc; FAAS; Polyurethane

## 1. Introduction

Zinc is an essential trace element of great importance for humans, plants and animals. It plays an important role in several biochemical processes and their compounds have bactericidal activity [1]. Zinc compounds have been employed in solutions as antiseptic and disinfectant agents. However, if it

is in excess, this metal can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress [2]. Waters from natural sources located in areas near to mining and smelters operation could be contaminated. Therefore, fauna, flora and soils that are in contact with these waters can also show high levels of zinc. Thus, zinc determination in natural waters, biological matrices, sediments, etc. is of great importance, considering that the concentration of this metal can serve as base

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for to characterise the level of pollution of a certain area.

Zinc concentrations in unpolluted natural waters are very low. So, very sensitive analytical techniques of detection are required as electrothermal atomic absorption spectrometry (ETAAS) [3,4] or inductively coupled plasma–mass spectrometry (ICP–MS) [5]. Inductively coupled plasma–optical emission spectrometry (ICP–OES) [6] and Flame Atomic Absorption Spectrometry (FAAS) [3] has not sufficient sensitivity for some determinations, so these techniques requires the use of a preconcentration step in order to reach an appropriate detection. Several enrichment procedures have been developed for determination of zinc traces in waters involving different analytical strategies such as precipitation [7] or liquid–liquid extraction [8].

On-line systems which solid-phase extraction (SPE) is involved always take place in two steps that involve sorption and elution. Many procedures of preconcentration can be found on literature employing a variety of materials, such as chelating [9] or polymeric [10,11] resins, ion-exchangers [12,13], functionalized silica [14,15], activated alumina [16,17] or carbon [18], fullerene [19] or polyurethane foam (PUF) [20,21]. Zinc determinations have been performed in on-line systems using solid-phase extraction with some materials cited above and spectrometric detection. Table 1 shows a comparison among on-line

procedures proposed for zinc preconcentration using solid-phase extraction.

Unloaded PUF was recently introduced in on-line separation and preconcentration systems [22,23]. Application of PUF in these produces smaller resistance for fluid passage than materials often employed for this proposal. Thus, it results low overpressure in the system reducing risk of leakage [24]. PUF is easily disposable, very low cost and simple preparation. Moreover, this sorbent is resistant to rough changes on pH conditions, despite to swell when in presence of some organic solvents concentrated, as ethanol. Some reviews about PUF have been described on literature [25–27].

Azo reagents have been used in spectrophotometric determinations due their capacity to form complexes with a large variety of metals [28]. Sorption of these reagents in PUF is a good alternative for enrichment procedures [25].

In the present paper, an on-line system for enrichment and determination of zinc by FAAS is proposed, using a minicolumn of polyurethane foam loaded with 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTABr) reagent. Me-BTABr was firstly synthesised, purified and characterised by our research group [29]. The aim of this work was to develop an analytical system capable to determining zinc at low levels, exploring the high selectivity of the FAAS technique.

Table 1  
Procedures for on-line preconcentration and determination of zinc

Sorbent	Sample	EF	CE (min <sup>-1</sup> )	<i>f</i> (h <sup>-1</sup> )	DL (μg l <sup>-1</sup> )	R.S.D. (%)	Detection	Reference
Silica C <sub>18</sub>	Seawater	60	30	30	0.5	6.5	FAAS	[15]
PUF	Natural water	15	4	17	0.85	6.0	FAAS	[33]
Chelex-100	Natural water	50	5	6	–	–	FAAS	[34]
Chelex-100	–	50	50	60	0.04	3.2	FAAS	[35]
CPG-8Q	–	87	87	60	0.03	2.6	FAAS	[35]
Silica DPTH	Seawater	–	–	40	1.7	–	ICP–OES	[36]
Amberlite XAD-2	Natural water	60	12	12	0.030	–	ICP–OES	[37]
CPPI	Natural and tap water	49	16	20	0.08	4.0	ICP–OES	[38]
PUF	Biological matrices	8	3	20	0.9	1.2	Spectrophotometry	[22]
Silica C <sub>18</sub>	Pharmaceutical preparations	–	–	45	10	3.3	Spectrophotometry	[39]
PUF Me-BTABr	Natural water	23	18	48	0.37	5.9	FAAS	This work

DL, detection limit; *f*, sampling frequency; R.S.D., relative standard deviation, EF, enrichment factor; CE, concentration efficiency; CPPI, carboxymethylated poly(ethylenimine)poly(methylenepolyphenylene) isocyanate; PUF, polyurethane foam; DPTH, 1,5-bis(di-2-pyridyl)methylene thiocarbonylhydrazide; FAAS, flame atomic absorption spectrometry; ICP–OES, inductively coupled plasma optical emission spectrometry.

## 2. Experimental

### 2.1. Apparatus

A Varian Model SpectrAA 220 (Mulgrave, Vic., Australia) flame atomic absorption spectrometer was used for the analysis. The zinc hollow cathode lamp was run under the conditions suggested by the manufacturer (current: 5.0 mA). Also the wavelength (213.9 nm), the bandwidth of the slit (0.5 nm) and burner height (13.5 mm) had conventional values. The flame composition was acetylene (flow rate  $2.01 \text{ min}^{-1}$ ) and air (flow rate  $13.51 \text{ min}^{-1}$ ). Nebulizer flow rate range suggested by the manufacturer is  $4\text{--}6 \text{ ml min}^{-1}$ . The value used was  $5.0 \text{ ml min}^{-1}$ .

An Alitea C-6 XV (Stockholm, Sweden) peristaltic pump furnished with Tygon tubes was used to propel all solutions. A Rheodyne 5041 (Cotati, CA, USA) model four-way manual valve was used to select preconcentration/elution steps. All connections were made using fittings, unions and tees made of plastic and PEEK materials. The manifold was built up with PTFE tube of 0.5 mm bore.

A Digimed DM 20 (Santo Amaro, Brazil) pH meter was also used.

### 2.2. Reagents

Ultrapure water from an Easypure RF water purification system (Barnstead, Dubuque, USA) was used to prepare all solutions. The hydrochloric acid was Suprapure (Merck, Darmstadt, Germany). All other reagents were of analytical reagent grade. The laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with ultrapure water and dried in a dust-free environment. The following solutions were used:

Zinc(II) solution ( $1000 \mu\text{g l}^{-1}$ ) was prepared by diluting a  $1000 \mu\text{g ml}^{-1}$  zinc solution (atomic absorption, Aldrich) with a  $1.0 \text{ mol l}^{-1}$  hydrochloric acid solution.

Tris buffer solution (pH 7.0) was prepared by dissolving 12.10 g of tris-(hydroxymethyl) amino-methane (Merck) in 1000 ml of deionized water and pH was adjusted with hydrochloric acid.

Hydrochloric acid ( $1.0 \text{ mol l}^{-1}$ ) was prepared by direct dilution with deionized water from the concentrated suprapur solution.

Polyurethane foam (PUF), commercial open-cell polyether-type polyurethane foam (by Atol of Brazil), was ground in a domestic blender with a large amount of deionized water, as previously described [30,31]. Afterwards, PUF was filtered off in a vacuum system and squeezed between clean sheets of filter paper. So, PUF was placed to dry in a stove at  $80^\circ\text{C}$  for 1 h and stored in a dark bottle.

Me-BTABr solution (0.05% (w/v)) was prepared by dissolving 0.10 g of 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol in 200 ml of absolute ethanol (Merck).

### 2.3. Synthesis of Me-BTABr

Me-BTABr was obtained by coupling diazotized 6-methyl-2-aminobenzothiazole with 4-bromophenol in acid solution at  $0\text{--}5^\circ\text{C}$  as described previously [29]. 6-Methyl-2-aminobenzothiazole was dissolved (4.92 g) in 50 ml of a  $6 \text{ mol l}^{-1}$  hydrochloric acid solution. To this solution was added dropwise a solution of 2.10 g of sodium nitrite in 20 ml of water at  $0\text{--}5^\circ\text{C}$  and the mixture was stirred and kept at  $0\text{--}5^\circ\text{C}$  for 1 h. For coupling, 5.20 g of 4-bromophenol was added to 20 ml of a  $1 \text{ mol l}^{-1}$  sodium carbonate solution and the mixture was cooled to  $0\text{--}5^\circ\text{C}$ . This solution was added dropwise to the above diazotized solution with vigorous stirring. The system was allowed stand overnight in refrigerator at  $4^\circ\text{C}$ . The reddish colour precipitate formed was filtered and purified by recrystallization with isopropyl alcohol.

### 2.4. Column preparation

The 0.05% (w/v) Me-BTABr solution was percolated through a laboratory-made cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm containing about 0.10 g of polyurethane foam at a flow rate of  $2.50 \text{ ml min}^{-1}$  for 5 min. Afterwards, the column was washed with a 10% (w/v) sodium hydroxide solution until the red effluent became colourless to remove the excess of Me-BTABr. Then, the column was washed with 5% (v/v) nitric acid solution and deionized water, respectively, using the same flow rate. Washing with nitric acid was necessary in order to prevent any metal contamination. All columns prepared by this way have shown good reproducibility.

It was proved by precision of the signals obtained for different columns.

### 2.5. Sample preparation

The following certified reference materials (CRMs) were analysed: IAEA (MA-B-3/TM) Fish Tissue and NIST 1547 Peach Leaves. For their decomposition [11], about 0.3 g of material was treated with 4.0 ml of 1:1 (v/v) nitric acid solution and kept overnight in Teflon vessel. Afterwards the Teflon vessel was closed and put into a pressurised digestion system. The thermal heating was carried out in a stove at 150 °C for 16 h. After cooling at room temperature these solutions were adjusted to pH 7.0 with a 10% (w/v) sodium hydroxide solution and a Tris buffer solution. After the volume was made up to 100 ml and diluted conveniently.

Natural water was sampled at Pituáçu lagoon at Salvador, BA. Seawater was taken from beaches also at Salvador City. For these samples, the only pre-treatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the Zn(II) ions on the flask walls. Afterwards, the samples were filtered and 50 ml of the filtrate were taken and the pH was adjusted to 7.0 by addition of 5 ml of tris buffer solution. The volume was then made up to 100 ml. At least one blank solution was run for each sample in order to evaluate zinc contamination by the reagents used.

### 2.6. On-line preconcentration system

The diagram of the on-line preconcentration system is shown in Fig. 1. The flow system was made up of a peristaltic pump fitted with Tygon tubes, a four-way valve and a minicolumn packed with polyurethane foam resin loaded with Me-BTABr, coupled to a flame atomic absorption spectrometer (FAAS). The flow system was operated in a time-based mode. A sample solution (S) containing zinc was kept at pH 7 with a Tris buffer solution and was pumped at 6.0 ml min<sup>-1</sup> percolated through a minicolumn that retained the cation. Then, zinc(II) ions are retained by chemical sorption as Me-BTABr complex and the remaining solution was discharged (W). By switching the injection valve a stream of 0.10 mol l<sup>-1</sup> hydrochloric acid (E) that flows at 5.5 ml min<sup>-1</sup> displaces the zinc ions. This elu-

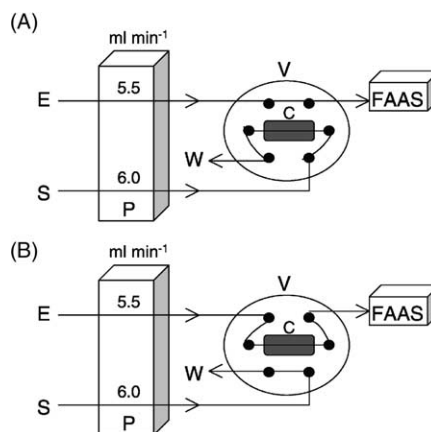


Fig. 1. Schematic diagram of the flow system used to preconcentration and determination of zinc by FAAS; S, sample; E, eluent; P, peristaltic pump; C, polyurethane foam/Me-BTABr minicolumn; V, four-way valve; FAAS, flame atomic absorption spectrometer and W, waste. A, four-way valve in the preconcentration step and B, four-way valve in the elution position.

ate was taken direct to the nebulizer–burner system of the spectrometer. For measurement of the signals, peak height and peak area were evaluated in the same injections. With peak area, the system shown a short increase in sensitivity. However, the use of peak height is advantageous, because the precision was better, specially in low concentrations. So, peak height was measured for subsequent experiments by using instrument software. It was read four times and averaged. It was not necessary to recondition the minicolumn at the end of each cycle since samples were buffered before preconcentration. Achieved sampling rate was 48 samples per hour for preconcentration time of 60 s and elution time of 15 s.

## 3. Results and discussion

To determine the best chemical and hydrodynamic conditions for zinc determination, the continuous flow system was optimized. A zinc solution containing 10.0 µg l<sup>-1</sup> was employed for these studies.

### 3.1. Chemical variables

The lifetime of column packed with Me-BTABr reagent immobilized on polyurethane foam was

monitored. It was made by measuring the signal of a  $10.0 \mu\text{g l}^{-1}$  zinc solution at end of each day of work and counting the number of cycles. Results show that column has good performance for at least 500 cycles. This indicates that material is very stable even under rough changes of pH conditions.

The effect of the sample pH on the zinc response was investigated within the range of 1.5–10.0. Maximum retention occurred within the pH range of 6.5–9.2. Then, pH range of 7.0–7.5 was selected for subsequent work, because the use of lower pH values gives rise to more selective determinations.

Sorption of zinc in column occurs under neutral to basic conditions. So, elution of zinc from the sorbent material was studied with acidic solutions. For this experiment, hydrochloric acid solutions at different concentrations ( $0.005$ – $2.00 \text{ mol l}^{-1}$ ) were used as stripping agent. Column was reconditioned with Tris buffer solution pH 7 after each elution due to use of relative high concentrated acid solutions. Total elution was reached in concentrations over  $0.05 \text{ mol l}^{-1}$ . So,  $0.10 \text{ mol l}^{-1}$  hydrochloric acid was selected as eluent for further studies. Furthermore, when used diluted eluent, such as  $0.10 \text{ mol l}^{-1}$  hydrochloric acid, signals did not show any difference, with and without reconditioning. Buffer added in the samples and standards was sufficiently strong to maintain the column

at an adequate pH condition for the preconcentration after each elution with acid. Then, reconditioning was not used in further studies to increase the system performance.

### 3.2. Hydrodynamic variables

Sample flow rate can affect the analytical signal in the proposed system. The effect of this parameter was also studied by varying flow rates from  $1.0$  to  $11.0 \text{ ml min}^{-1}$ . As the amount of sample varies with flow rate if preconcentration time is constant, for this experiment, a volume of  $3.00 \text{ ml}$  of a zinc solution was pumped in order to maintain the sample amount invariable. Analytical signals decreased slightly at high flow rates, upper  $6.5 \text{ ml min}^{-1}$ , as can be seen in Fig. 2. These results indicate that the zinc sorption is minor at high flow rates because zinc(II) ions passes by column too quickly that the contact time between the phases is not sufficient for a significant retention. Moreover, high flow rates increases back-pressure and this could cause leakage. Thus, a flow rate of  $6.0 \text{ ml min}^{-1}$  was chosen for posterior experiments as a compromise between efficiency and stability of system.

In order to determinate the retention efficiency,  $10.0 \text{ ml}$  of a  $10.0 \mu\text{g l}^{-1}$  zinc solution was percolated

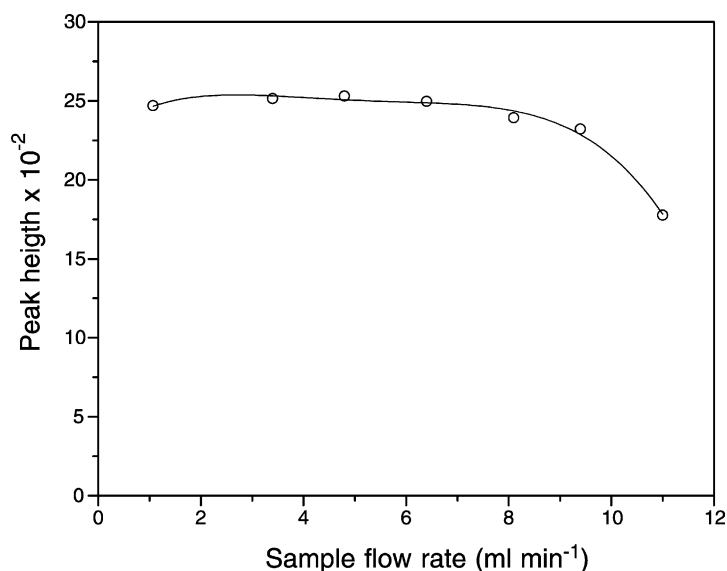


Fig. 2. Effect of sample flow rate in the preconcentration and determination of zinc by FAAS.

by the column. The desorption was carried out with 1.00 ml of 0.10 mol l<sup>-1</sup> hydrochloric acid solution and measured by FAAS. In these conditions, the retention efficiency of the column, defined as the ratio between the analyte mass in original sample and that in the concentrate, was 0.87.

The effect of the eluent flow rate in the step of zinc desorption from the minicolumn was also investigated. Results showed that the analytical signal is maximum and constant at flow rates within the range of 3.5–7.0 ml min<sup>-1</sup>. At flow rates less than 3.5 ml min<sup>-1</sup> the analytical signal considerably decreased, resulting broader peaks. Probably, it is due to incompatibility between elution and nebulization flow rates, which cause significant dispersion when eluent flow rate is very smaller than nebulizer flow rate. This experiment was repeated but now determining the retention efficiency of the zinc to each eluent flow rate. All the results obtained are not shown significant difference, which demonstrates that the zinc desorption is fast and independent of the elution flow rate. Thus, a flow rate of 5.5 ml min<sup>-1</sup> was selected in the subsequent studies, in order to match elution and aspiration flow rates.

In some preconcentration systems there is the possibility of improving sensibility by increasing the sample volume. In time-based flow injection systems, this can be increasing the preconcentration time. The performance of the flow system was investigated varying the preconcentration times from 0.5 to 3.0 min. The FAAS analytical signal increased proportionally with the preconcentration time, what means that the retention efficiency [13] was constant within this time interval. If more sensitive determinations are required, preconcentration time can be increased if not exceeding the limit of 3.0 min. Despite, a preconcentration time of 1 min was chosen to combine sensitivity and efficiency.

### 3.3. Effect of foreign ions

Solutions containing zinc (10.0 µg l<sup>-1</sup>) and other ions in order to determine the selectivity of analytical system were prepared and the developed procedure was applied. The effect of each species was considered interference when the signal in the presence of the species resulted in signal depression by 5%. The following ions in the concentrations in the brackets:

Na<sup>1+</sup> (15 g l<sup>-1</sup>), K<sup>+</sup> (1 g l<sup>-1</sup>), Al<sup>3+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> (50 µg l<sup>-1</sup>), Fe<sup>3+</sup> (500 µg l<sup>-1</sup>), Cd<sup>2+</sup> and Cu<sup>2+</sup> (100 µg l<sup>-1</sup>), Ni<sup>2+</sup> and Co<sup>2+</sup> (50 µg l<sup>-1</sup>), PO<sub>4</sub><sup>3-</sup> (150 µg l<sup>-1</sup>), NO<sub>3</sub><sup>-</sup> (1 g l<sup>-1</sup>), SO<sub>4</sub><sup>2-</sup> (0.50 g l<sup>-1</sup>) and Cl<sup>-</sup> (15 g l<sup>-1</sup>) do not interfere in the determination of zinc. These data are not the limits. Other concentrations could be tested.

### 3.4. Analytical features

The solid-phase flow system allowed the determination of zinc in the concentration range of 0.37–40.00 µg l<sup>-1</sup> for 1 min of preconcentration time. The calibration graph under the optimum chemical and flow conditions with the manifold depicted in Fig. 1, was given as  $A = 0.01981 + 0.02222C$  in the interval of 0.37–40.00 µg l<sup>-1</sup> ( $C$  is zinc concentration in solution, µg l<sup>-1</sup>). By using direct aspiration in FAAS without the preconcentration system the linear range was between 4.0 and 1500 µg l<sup>-1</sup> ( $A = 0.00516 + 0.5059C$ ). The experimental preconcentration factor [13,32] calculated as the ratio of the slopes of the calibration graphs with and without preconcentration was 23 for 1 min of preconcentration time.

The precision of the procedure, determined as the relative standard deviation (R.S.D.) in sample solutions containing between 1.0 and 10.0 µg l<sup>-1</sup> of zinc was in the range of 5.9–1.8%, respectively, calculated by seven measurements.

The detection limit (DL), defined as the zinc concentration that gives a response equivalent to three times the standard deviation ( $\sigma$ ) of the blank ( $n = 11$ ), was found to be 0.37 µg l<sup>-1</sup> in 6.0 ml of sample solution.

The concentration efficiency [13], defined as the preconcentration factor of an analyte achieved by the system in 1 min was also calculated. It is 18 min<sup>-1</sup>.

### 3.5. Accuracy of the method

In order to evaluate the accuracy of developed procedure, the following certified reference materials were analysed: IAEA (MA-B-3/TM) Fish Tissue and NIST 1547 Peach Leaves. The results are described in Table 2. Confidence intervals are at 95% level. It was found that there is no significant difference between

Table 2  
Zinc determination in certified reference materials

Sample	Zinc amount ( $\mu\text{g g}^{-1}$ )	
	Proposed methodology	Certified
Fish tissue MA-B-3/TM IAEA	$113.2 \pm 5.1$	$109.2 \pm 2.8$
Peach Leaves NIST 1547	$18.7 \pm 0.5$	$17.9 \pm 0.4$

IAEA, International Atomic Energy Agency, Monaco. NIST, National Institute of Standards and Technology, USA.  $n = 3$ .

achieved results by proposed method and certified results.

### 3.6. Application

The analytical system was used for zinc determination in natural water samples. The results are described in Table 3. Recoveries ( $R$ ) of spike additions (0.2 or  $1.0 \mu\text{g g}^{-1}$ ) to several water samples were quantitative (92–108%).  $R$  was calculated as follows:  $R$  (%) =  $\{(C_m - C_o)/m\} \times 100$ . Where  $C_m$  is a value of zinc in a bland sample (a spike sample),  $C_o$  is a value of zinc in a sample and  $m$  is the amount of zinc spike. These results proved also that the procedure is not affected by high concentrations of alkaline and alkaline earth metals and can be applied satisfactorily for zinc determination in water and biological material.

Table 3  
Results obtained for zinc determination in natural water samples

Sample	Added ( $\mu\text{g l}^{-1}$ )	Zinc found by methodology proposed ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>	Recovery (%)
Lagoon 1	0.0	$4.54 \pm 0.25$	–
	2.5	$7.05 \pm 0.08$	100
	7.5	$12.60 \pm 0.31$	108
Lagoon 2	0.0	$7.34 \pm 0.45$	–
	2.5	$9.90 \pm 0.42$	102
	7.5	$14.51 \pm 0.33$	96
Seawater 1	0.0	$3.29 \pm 0.39$	–
	2.5	$5.95 \pm 0.12$	106
	7.5	$11.03 \pm 0.54$	103
Seawater 2	0.0	<DL	–
	2.5	$2.70 \pm 0.37$	108
	7.5	$6.88 \pm 0.29$	92

DL, detection limit.  $n = 3$ .

<sup>a</sup> Confidence interval 95%.

## 4. Conclusion

The proposed flow injection system with on-line preconcentration by minicolumn packed with PUF/Me-BTABr is a good alternative for zinc determination in water and biological samples. The developed manifold permitted high sample flow rates in order to achieve good sensitivity. This method proved to be rapid, reliable and flexible with limited interference. The proposed procedure has analytical performance comparable to other procedures for zinc determination described on the literature, as can be seen in the Table 1. High sample throughput (48 samples per hour) is a great advantage of this procedure if compared to many methods existing to zinc preconcentration. Such characteristic is very important and of practical interest for routine laboratories equipped just with FAAS for element analysis. The low detection limit ( $0.37 \mu\text{g l}^{-1}$ ) is also very interesting for zinc determination in a large range of samples.

The combination of FAAS with flow injection system using supports loaded with complexing reagents can be a promising way in preconcentration and determination of cations in a wide range of samples. The enrichment factor and the detection limit of the procedure can be further improved by increasing preconcentration time without degradation in the efficiency due to the favourable kinetics and low hydrodynamic impedance of the present system.

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