J. Braz. Chem. Soc., Vol. 8, No. 1, 39-45, 1997.
Printed in Brazil.

0103 - 5053 $6.00 + 0.00

Article

On-line Microwave-Assisted Sample Decomposition for Lead Determination in Fish Slurry Samples by Electrothermal Atomic Absorption Spectrometry

Marco A.Z. Arruda*[+], Anne H. Fostier and Francisco J. Krug

Centro de Energia Nuclear na Agricultura, Universidade de S. Paulo, C.P. 96, 13418-260 Piracicaba - SP, Brazil

Received: January 19, 1996; September 10, 1996

Um procedimento FIA envolvendo decomposição em linha auxiliada por microondas foi proposto para a determinação de chumbo em peixes por espectrometria de absorção atômica com atomização eletrotérmica. Um volume de 300 μL da amostra em forma de suspensão foi injetado simultaneamente com 400 μL de ácido nítrico (6 mol L^{-1}), e a mistura foi dirigida para um reator tubular posicionado dentro do forno de microondas. A amostra processada foi coletada em uma cubeta do amostrador de um espectrômetro de absorção atômica com forno de grafite. A curva analítica mostrou-se linear entre 2,5 e 25,0 μg L^{-1} Pb e o limite de detecção foi determinado como 0,72 μg L^{-1}. A precisão, expressa em desvio padrão relativo, foi de 10,5% (n = 20) para repetibilidade e de 14,3% (n = 10) para reprodutibilidade. A exatidão do método foi confirmada empregando-se um material de referência e comparando-se os resultados obtidos com um procedimento envolvendo decomposição nítrico-perclórica.

An on-line microwave-assisted decomposition procedure for the determination of lead in fish is proposed. 300 μL slurry and 400 μL of a 6 mol L^{-1} HNO_3 solution were simultaneously injected, and the mixture was positioned inside a microwave oven. The decomposed sample inside the flushing solution was collected in the autosampler cup of a graphite furnace. The proposed procedure covered the 2.5 to 25 μg L^{-1} Pb range and presented a detection limit of 0.72 μg L^{-1} Pb. Precision expressed as RSD, was 10.5% (n = 20) for repeatability and 14.3% (n = 10) for reproducibility. Accuracy was assessed using standard reference material, and also by comparing the results to a nitric-perchloric decomposition procedure.

Keywords: *on-line microwave decomposition, fish analysis, lead determination, electrothermal atomic absorption spectrometry*

Introduction

The content of lead in the environment and food is of great concern because it is recognized as a cumulative poison in animals and humans. Lead intake by humans has been estimated at 200-300 μg per day, varying as a function of the degree of contamination. Usually food is responsible for up to 70% of daily lead intake[1].

The toxicity of lead in humans and animals is usually chronic because it is excreted more slowly than it is absorbed, resulting in an accumulation in various tissues. Symptoms of lead poisoning include irritability, anorexia, malaise, and headaches. Depending on the degree of intoxication, constipation and attacks of abdominal pain (lead colic) may be observed. Children are more susceptible to lead poisoning because they absorb a higher percentage of lead through the gastrointestinal tract, have more hand-to-mouth activity, and have developing nervous systems that are more sensitive to lead[2-4].

In monitoring and health risk evaluation programs, the number of environmental and biological samples is often high, and the sample preparation steps become a limiting factor for analysis, mainly in terms of the time required and problems of contamination. Slurry sampling is a good

[+] Present address: Departamento de Química Analítica, Universidade de Campinas, C.P. 6154, 13083-970 Campinas - S. Paulo, Brazil

choice for circumventing these problems, and this technique has been successfully used for direct introduction of samples in atomic spectrometry[5-7] and introduced directly into the atomization system by means of flow injection systems[8,9]. In some instances, however, the elements to be determined are not easily atomized from solid particles because of the complexity of the matrix, and a pre-treatment step is required. An alternative for circumventing this problem is the use of a microwave technique as a heat source for sample decomposition, thus reducing the time required for solubilization and losses of volatile elements.

Coupling continuous flow systems with microwave digestors has been carried out in combination with flame atomic absorption[10-12] or inductively coupled plasma atomic emission spectrometry[13,14]. However, few applications with electrothermal atomic absorption spectrometry have been reported[15,16]. The state of the art and the features of several slurry techniques proposed for lead determination[17,29] are summarized in Table 1.

The present paper describes a simple and fast procedure which exploits an on-line decomposition of slurry samples coupled to a flow injection system. The effectiveness of the method was evaluated by determining lead in fish samples.

Experimental

Apparatus

A Perkin-Elmer model 4100 ZL atomic absorption spectrometer equipped with a longitudinal Zeeman background corrector and a pyrolytically coated transversely heated graphite atomizer with an integrated L'vov platform

Table 1. Features of slurry sampling techniques for the determination of lead in food samples by atomic spectrometric techniques.

Detection	Application	RSD (%)	Suspensions			Ref.
			Stabilizer	Particle Size	Concentration	
HGAAS	Anchovies	4.2	Triton X-100	-	2-10% (m/v)	17
ETAAS	Biscuit	27.3	Ethanol-H_2O_2	-	-	18
ETAAS	Bovine liver	54.0	Antifoam B emulsion	< 50 μm	10% (m/v)	19
ETA-LE-AFS	Bovine liver	-	Triton X-100	-	0.2% (m/v)	20
ETAAS	Bread cereals	44.4	Ethanol-H_2O_2	-	-	18
ETAAS	Brussel sporuts	-	Viscalex HV-30	-	-	21
ETAAS	Fish	13.6	Antifoam B emulsion	< 50 μm	10% (m/v)	19
ETAAS	Fish	13.0	Glycerine-methanol-HNO_3	-	15-300 μg in 5 μL of slurry	22
HGAAS	Hay	4.3	Triton X-100	< 25 μm	-	23
HGAAS	H-9 whole total diet	10.0	Triton X-100	< 25 μm	2-10% (m/v)	24
ETAAS	Kale	10.0	Antifoam B emulsion	< 50 μm	10% (m/v)	19
HGAAS	Lettuce	13.8	Triton X-100	< 25 μm	-	23
HGAAS	Lettuce	5.6	Triton X-100	-	2-10% (m/v)	17
HGAAS	Lettuce	5.5	Triton X-100	< 25 μm	2-10% (m/v)	24
ETAAS	Milk powder	-	-	-	-	25
HGAAS	Mussels	7.9	Triton X-100	< 25 μm	-	23
ETA-LE-AFS	Non-fat milk powder	-	Triton X-100	-	0.2% (m/v)	20
ETAAS	Paprika	2.7-6.7	Ethanol-H_2O_2	< 30 μm	0.05-0.4% (m/v)	26
ICP-AES	Pepper	1.6-3.8	Triton X-100	5-3.5 μm	0.5% (m/v)	27
ICP-MS	Rice flour	-		< 3 μm		28
HGAAS	Sardines	7.1	Triton X-100	-	2-10% (m/v)	17
ETAAS	Spinach	3.0	Viscalex HV30	1-50 μm	up to 10% (m/v)	29
ETAAS	Spinach	10.6	Glycerine-methanol-HNO_3	-	15-300 μg in 5 μL of slurry	22
ETAAS	Wheat flour	28.6	Ethanol-H_2O_2	-	-	18

HGAAS: hydride generation atomic absorption spectrometry; ETAAS: electrothermal atomic absorption spectrometry; ETA-LE-AFS: electrothermal atomizer-laser excited-atomic fluorescence spectrometry; ICP-AES: inductively coupled plasma atomic emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry.

(Perkin-Elmer part n B050-4033) and an AS-71 furnace autosampler were used. The wavelength was set at 283.3 nm using a Perkin-Elmer EDL II system as the radiation source with a 0.7 nm spectral bandwidth. The integrated absorbance was used, and the results were recorded on an Epson LQ-870 printer. The furnace program is shown in Table 2. A mixture of 90% Ar and 10% H_2 v/v was employed as the purge gas.

The flow system comprised an Ismatec mp13GJ4 peristaltic pump with Tygon pumping tubes, a laboratory-made three-piece injector commutator[30] with built-in T-shaped connectors, poly(tetrafluoroethylene) (PTFE) transmission lines of 0.8 mm i.d., and a model CEM MDS-81D microwave oven, equipped with a magnetron of 2450 MHz with a nominal maximum power of 700 W. The digestion coil was introduced into the microwave oven through the pressure and temperature sensor holes. A Hewlett-Packard 8451A diode-array spectrophotometer equipped with a conventional quartz cell was used to verify the stability of the slurries.

Reagents

All reagents were of analytical grade, and distilled/deionized water was used. Nitric acid was distilled in a quartz sub-boiling still (Kürner). The 1000 mg L^{-1} Pb stock solution was prepared from lead nitrate (Johnson & Mattey, Co.) in 0.1% v/v HNO_3. The reference solutions containing 2.5-25 μg L^{-1} Pb were prepared by serial dilutions of the stock solution with 2.4 mol L^{-1} HNO_3. Mix of 0.003 mg of $Mg(NO_3)_2$ plus 0.05 mg of $NH_4H_2PO_4$ was used as a chemical modifier and Triton X-100 scintillation grade (Amersham/Searle) was employed to stabilize the slurry samples.

The effect of concomitants was evaluated using a lead reference solution containing 10 μg L^{-1} in 2.4 mol L^{-1} HNO_3 without the concomitants, or in the presence of 2 mg L^{-1} Fe, 2 mg L^{-1} Zn, 300 mg L^{-1} Cl^-, 400 mg L^{-1} K, 300 mg L^{-1} Na, or 90 μg L^{-1} Cu.

Sample preparation

The fish samples, collected in the Amaparí river (Amapá, Brazil), were ground with a mixer in order to make a slurry. After being frozen for five days, the resulting slurry was lyophilized by freeze-drying at 6 Pa for 48 h up to a constant weight. The resulting lyophilized samples were sieved through a standard nylon sieve in order to obtain a particle size ≤ 200 μm. Then an accurately weighed amount of about 250 mg was mixed with 3 mL of 2.4 mol L^{-1} HNO_3 and 1 mL of 0.25% v/v Triton X-100, and the volume was completed to 5 mL with 2.4 mol L^{-1} HNO_3. Agitation for 20 min in an ultrasonic bath was necessary to homogenize the slurry sample. Standard Reference Material MA-A-2 n 1062/TM - Fish homogenate

Table 2. The furnace program for the determination of Pb; injected volume, 20 μl of sample + 10 μL modifier.

Step	Temperature (°C)	Time (s)		Gas flow rate (mL min^{-1})
		Ramp	Hold	
Dry1	130	20	35	250
Dry2	160	20	25	250
Pyrolysis	850	10	20	250
Atomization	1500	0	5	0
Clean	2600	1	2	250

Program time: 138 s; Injection temperature: 100 °C.

(International Agency of Energy Atomic) was used to check the accuracy of the proposed procedure.

Additionally, and for the purposes of comparision, the samples also underwent nitric-perchloric digestion. Each fish sample was accurately weighed (0.4-0.5 g, dry weight) and transferred together with 10 mL of concentrated nitric acid, to a 75 mL conical flask. After complete dissolution (*ca.* 2 h), the flask was placed on a hot plate at 160 °C until a clear solution was obtained. Next, 2 mL of perchloric acid was carefully added to the flask and the temperature was increased to 210 °C. The decomposition was completed with the appearance of white fumes and approximately 0.5 mL solution remained. The decomposed sample was then transferred to a 10 mL volumetric flask, and diluted to mark with 2.4 mol L^{-1} HNO_3.

Procedure

The flow system for on-line fish decomposition is illustrated in Fig. 1. In the position specified, both loops, loaded with 300 μL sample and 400 μL digestion solutions (6 mol L^{-1} HNO_3), were inserted into the air carrier streams at 2 mL min^{-1} and driven towards the confluence point (X); the mixed solution was then directed towards the 500 cm PTFE digestion coil (0.8 mm i.d.) located inside the microwave oven. The coil was wrapped around an Erlenmeyer flask filled with water, which assured a volume (150 mL) inside

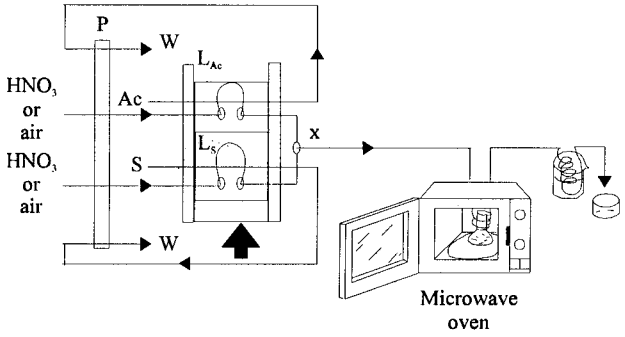

Figure 1. The FI-microwave oven-ETAAS system for the determination of lead in fish samples. L_S and L_{Ac} are the sample (300 μL) and nitric acid (400 μL) loops, respectively, and W is waste. Air flow rate, 2 mL min^{-1}.

the cavity sufficient to prevent damage in the magnetron. About 50 s after sample injection, when the entire sample plug was flowing inside the digestion coil, the peristaltic pump was stopped and the microwave program (Table 3) was started. After the microwave action, the pump was re-started and a 0.1% v/v HNO_3 solution was introduced via the tube of the air carrier in order to clear the residual decomposed sample and to transport the sample to the autosampler cup which was completely filled (total volume, 1 mL). A 150 cm coil immersed in a water-filled beaker was incorporated into the flow system to allow the expansion of digestion fumes. The same procedure was followed for the blanks. After the processing of each sample, the air carrier streams were introduced into the flow manifold again in order to remove the residual washing solution.

Results and Discussion

The stability of the slurries

In order to check the stability of the slurry sample, an experiment was carried out[31] using a diode-array spectrophotometer to record changes in the turbidimetry of the fish sample. Fig. 2 shows the variation in the absorbance measured at 500 nm for a slurry containing 250 mg fish sample dispersed in 4 mL of 2.4 mol L^{-1} HNO_3 plus 1 mL of 0.25% v/v Triton X-100. The change in absorbance was monitored for 6 minutes and its variation was 20%. However, when this change was measured for 5 min only 13% was observed, indicating that this condition is sufficient for the sample preparation. Without a thixotropic agent, changes in absorbance of up to 50% were detected for this type of sample.

As the time necessary to fill the sample loop of the flow system was about 30 s, the time during which the slurry remained stabilized was sufficient.

Table 3. The microwave oven program for fish sample digestion.

Power(W)	350	0	350	0	350	0	350
Time (s)	120	20	120	20	120	20	120

Total time: 540 s; Digestion time: 480 s.

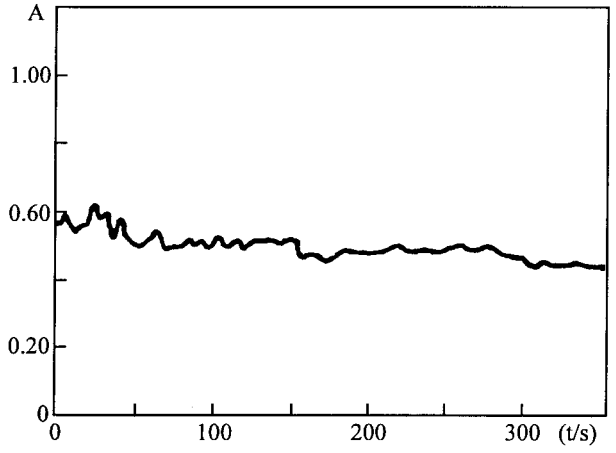

Figure 2. The temporal variation of the absorbance at 500 nm of 250 mg of fish sample dispersed in HNO_3 (*ca.* 4 mL) plus 1 mL 0.25% v/v Triton X-100.

Furnace heating conditions

The furnace program (Table 2) included a hot injection procedure and two temperature ramps in order to guarantee soft and totally dry conditions of the sample, to avoid problems from matrix effects. Also, a 90% Ar plus 10% H_2 v/v mixture was used as the purge gas because it increases the dissociation of the lead molecular species in the gas phase and reduces matrix interferences[32].

In order to optimize the furnace conditions and to avoid lead loss during pyrolysis, use of chemical modifiers is an excellent choice. So, some chemical modifiers were tested: $NH_4H_2PO_4$, $Mg(NO_3)_2$, and $NH_4H_2PO_4 + Mg(NO_3)_2$. The situation without a modifier was also checked.

The experiment of the pyrolysis step was performed by maintaining the atomization temperature at 1500 °C and varying the pyrolysis temperature. In this experiment, the optimum heating conditions did not significantly differ in sensitivity, regardless of the different chemical modifiers. The loss of 10 μg L^{-1} lead standard solution was observed in the pyrolysis cycle at 900 °C for almost all chemical modifiers, except for the $NH_4H_2PO_4 + Mg(NO_3)_2$ mixture where analyte loss was observed only at 1100 °C. However, when using a decomposed fish sample with about 10 μg L^{-1} Pb the same behaviour was not observed. When the $NH_4H_2PO_4 + Mg(NO_3)_2$ modifier was used, losses of lead were observed at 900 °C. Therefore, the pyrolysis temperature chosen was 850 °C.

The digestion conditions for solid samples

Because of the lack of uniformity of microwave distribution[33,34] inside the oven, the best position for the digestion coil was determined by placing 14 glass beakers in different positions (Fig. 3), each containing 50 g of water. The microwave power selected was 700 W for 8 min. This experiment was made in quintuplicate, and the results of the weight loss were calculated by the difference between the weights of the water-filled beaker before and after microwave action, which ranged between 2.04 and 9.48 g. The best position found for the action of the microwave based on microwave power spatial distribution is shown in Fig. 3. These positions were at 35 and 6 cm, on the x and y axes, respectively.

Nitric acid was selected as the solubilizer, based on previous work[16]. In order to establish the required time and acid concentration for the optimization of the digestion conditions for total recovery of lead in the analysis of solid

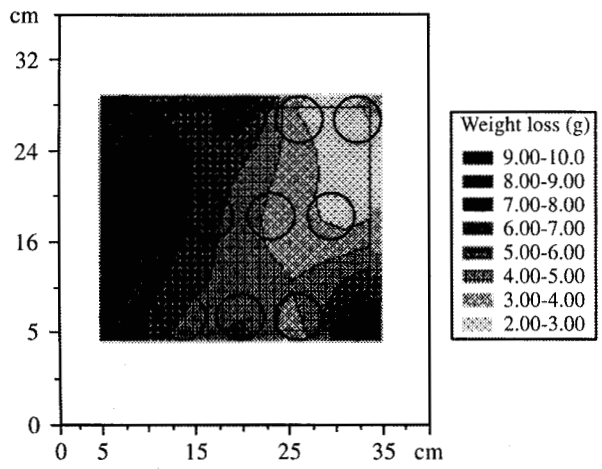

Figure 3. Influence of the position of the sample relative to the microwave magnetron on weight loss. Microwave power spatial distribution inside the oven for the influence of axes x and y (in cm) on weight loss.

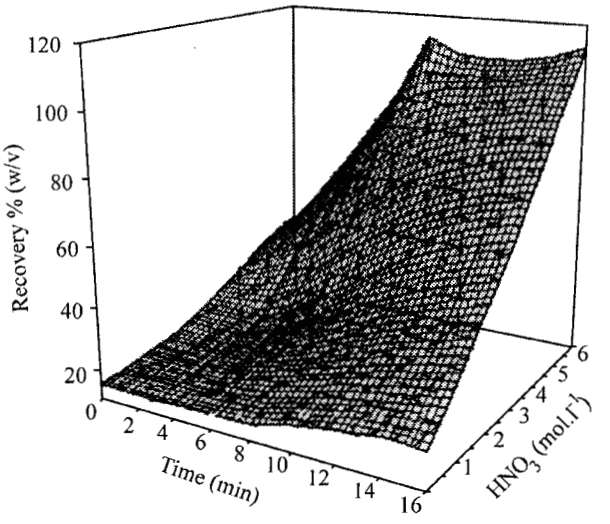

Figure 4. Response surface of the digestion conditions for lead recoveries in MA-A-2 Reference Material n° 1062/TM Fish Homogenate at variable digestion times and acid concentrations.

samples, a factorial experiment was carried out. In this context, an appropriate amount of 250 mg fish samples (Standard Reference Material MA-A-2 n 1062/TM, IAEA) was prepared as mentioned in the Sample Preparation Section, and then introduced into the above-mentioned flow system. Volumes of 300 µL for samples and 400 µL for the acid were injected into the flow system using a merging-zone approach[35]. The sample-injected volume was selected based on the sensitivity of the method. For smaller volumes, the sensitivity was not acceptable and erratic results were obtained (RSD > 25%). For optimization of digestion conditions, a power of 350 W was fixed, and the digestion time was varied between 0 and 16 min, while the acid concentration was varied between 0 and 6 mol L^{-1}. When microwaves were not applied, recovery was only 14.6, 23.1 and 37.7% for nitric acid concentrations of 0, 3, and 6 mol L^{-1}, respectively. Fig. 4 shows the response surface related to the digestion parameters. At 350 W, the time required to pretreat the fish samples was 8 min, an acceptable recovery value of 113% being obtained when 6 mol L^{-1} HNO_3 was used. It should be pointed out that higher acid concentrations were not used to avoid eventual damage of some parts of the digestion system, as well as of the injector commutator. In the microwave oven program (Table 3), three steps without microwave action, intercalated with other steps, were necessary to maintain the sample inside the oven, due to gas formation during microwave digestion.

No memory effect was observed by digesting a blank solution after a fish sample.

Analytical characteristics

A linear range (r = 0.999; n = 7) between 2.5 and 25.0 µg L^{-1} Pb was obtained using the optimized flow conditions in Fig. 1 and the furnace program shown in Table 2. The detection limit of 0.72 µg L^{-1} Pb, and the characteristic mass of 29.8 pg 0.0044 s^{-1}, were calculated using a 10 µg L^{-1} Pb standard solution according to IUPAC recommendation[36]. Precision was estimated by analyzing fish samples (*Sarrassalmus sp.*). Repeatability of 10.5% (n = 20) and reproducibility of 14.3% (n = 10) were calculated.

The effect of the concomitants was evaluated by analyzing the variations in the analytical responses of 10 µg L^{-1} standard solution in the absence and presence of some elements (Table 4). Measurements were made in triplicate, and the results showed that lead can be determined in a matrix of similar chemical composition. A maximum signal difference of ± 10% was attributed to the inherent uncertainties of the method.

Table 4. Tolerated levels of the concomitants in the determination of 10 µg L^{-1} Pb.

Concentration of the species (mg L^{-1})	Signal difference (%)*
2 Fe^{3+}	-10.0
2 Zn^{2+}	+7.0
0.09 Cu^{2+}	+6.0
400 K^{+}	+9.0
300 Na^{+}	-6.0
300 Cl^{-}	+9.7

* Percentage difference between the signals obtained in the presence and absence of the concomitant species.

Table 5. Lead content in lyophilized samples as determined by nitric-perchloric (Wet) and microwave decomposition (MW).

Popular names in Brazil	Scientific name	Concentration* ($\mu g.g^{-1}$)	
		Wet	MW
Piranha	*Serrassalmus* sp.	0.30 ± 0.03	0.29 ± 0.03
Pirarucu	*Arapaima gigas*	0.21 ± 0.02	0.23 ± 0.01
Cascudo	*Pterigo phichthys* sp.	0.19 ± 0.02	0.18 ± 0.02
Pescada branca	*Urophycis* sp.	0.20 ± 0.01	0.23 ± 0.01
Fish homogenate **	---	0.54 ± 0.01	0.57 ± 0.03

* Mean ± standard deviation (n = 5); ** IAEA MA-A-2 n 1062/TM Reference Material (certified value: 0.58 ± 0.07 $\mu g\ g^{-1}$).

Fish analysis

The accuracy of the proposed method was evaluated by analyzing fish homogenate material (certified lead concentration, 0.58 $\mu g\ g^{-1}$) and by comparing it with the wet digestion procedure[37] of fish samples using nitric and perchloric acids. The average of five consecutive determinations on individual test portions was 0.57 ± 0.03 $\mu g\ g^{-1}$. The results obtained by the proposed on-line microwave digestion system are summarized in Table 5. By applying the *t*-test, both sets of results were similar at a 95% confidence level, indicating the accuracy of the proposed on-line slurry digestion method.

Conclusions

The proposed on-line microwave decomposition allows rapid fish slurry pre-treatment, the total time involved for the sample preparation and analysis not exceeding 25 min. No problems associated with high pressure were observed by collecting the digested fish sample in a open autosampler cup. The proposed system can be applied to other samples of similar or less complex chemical composition.

Acknowledgments

The authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brasília, Brazil), to A.L.D. Comitre for her collaboration in the stages of this research, and to E.A.G. Zagatto for language improvement.

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FAPESP helped in meeting the publication costs of this article