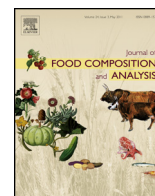


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## Original Research Article

# Synthesis and characterization of functionalized silica with 3,6-dithia-1,8-octanediol for the preconcentration and determination of lead in milk employing multicommuted flow system coupled to FAAS



Paulo A.B. da Silva <sup>a,b</sup>, Gustavo C.S. de Souza <sup>a,b</sup>, Dilmo M. da S. Leotério <sup>a,b</sup>,  
Mônica F. Belian <sup>a</sup>, Wagner E. Silva <sup>c</sup>, Ana P.S. Paim <sup>b</sup>, André F. Lavorante <sup>a,\*</sup>

<sup>a</sup> Departamento de Química, Universidade Federal Rural de Pernambuco, Rua Dom Manuel de Medeiros, S/N, Dois Irmão, 52171-900 Recife, PE, Brazil

<sup>b</sup> Departamento de Química Fundamental, Universidade Federal de Pernambuco, Av. Prof. Luiz Freire, S/N, Cidade Universitária, 50740-540 Recife, PE, Brazil

<sup>c</sup> Unidade Acadêmica do Cabo de Santo Agostinho, Universidade Federal Rural de Pernambuco, 54510-000 Cabo de Santo Agostinho, PE, Brazil

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## ABSTRACT

Novel functionalized silica, containing 3,6-dithia-1,8-octanediol (Si-DIO), was synthesized and characterized by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM) and nuclear magnetic resonance (NMR) of <sup>13</sup>C and <sup>29</sup>Si. The Si-DIO was used to pre-concentrate and determine the amount of Pb(II) in milk samples employing a multicommuted flow system coupled to flame atomic absorption spectrometry (FAAS). For the adsorption process, a pre-concentration minicolumn with 100 mg of Si-DIO, a solution of 0.005 mg L<sup>-1</sup> Pb(II) at pH 9.0 and HNO<sub>3</sub> as the eluent was used, obtaining an enrichment factor of 28 times with retention efficiency higher than 99%. The Pb(II) ion, using the multicommuted flow system coupled to FAAS, showed a linear response between 0.005 and 20.0 mg L<sup>-1</sup>; a linear coefficient where  $r = 0.9939$  and  $n = 7$ ; a detection limit estimated at 0.001 mg L<sup>-1</sup> and a relative standard deviation of 3.8% ( $n = 50$ ). Fifty pre-concentrations runs were tested in the minicolumn without significant variation in the analytical signal. The proposal system showed analytical applicability to determine Pb(II) ion in milk samples, presenting recovery of 90.7–102.5%.

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## 1. Introduction

The contamination of the environment and living beings with heavy metals over time has become a major problem for society. The toxic and accumulative effect of the heavy metals in the human body causes often irreversible damage. In most cases, damage happens through the ingestion of contaminated food and water (Chiron et al., 2003; Gonçalves et al., 2008). Thus, it becomes important to find a way for the efficient determination of heavy metal levels in food and water, aiming at their safe consumption.

The sources of Pb contamination may be attributed to natural sources and anthropogenic activities. Both the lead released in the environment due to industrial development and the urbanization process have resulted in an extensive contamination of soil, water, food and also living beings (Ahmed and Mamun, 2001; Oymak et al., 2009; Souza et al., 2007; Suleiman et al., 2008).

Lead cause serious damage to health, causing cardiovascular, gastrointestinal, hematologic and particularly neurological and renal problems (Organization, 1996). The World Health Organization (WHO) established a lead limit of 25.0 μg kg<sup>-1</sup> (equivalent to 3.5 μg kg<sup>-1</sup> of body weight per day) for human beings, considering this metal as a cumulative poison (ATSDR, 2007).

In this context, various silica materials (SM) have been synthesized, able to adsorb, pre-concentrate and determine Pb in different food matrices. Silica has been widely used because of its high surface area, mechanical and thermal properties, controlled morphology and the high reactivity of the silanol groups [13–14]. The modification of the silica surface with organic molecules has been the object of many studies. The use of a silylant agent to help bind the alkyl groups on the silica surface is a strategy viable for the generation of new hybrid materials. These organic–inorganic materials can exhibit different properties of increased interaction capacity with ions or molecules through chemical interaction (coordinative binding or intermolecular forces) and not purely physical (adsorption) (Galán-Cano et al., 2013; Najafi et al., 2011; Sharma et al., 2013; Xie et al., 2008) when

\* Corresponding author. Tel.: +55 81 33206375; fax: +55 81 33206375.  
E-mail address: aflavora@dq.ufpe.br (A.F. Lavorante).

compared with silica. A large number of adsorbent materials based on functionalized silica have been employed to determine lead in different types of samples (Aboufazeli et al., 2013; J.-C. He et al., 2013; Karve and Rajgor, 2007; Sabermahani et al., 2013).

Because of their higher sensitivity, a number of atomic spectrometry techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) (Xu et al., 2007; Zhao et al., 2012), inductively coupled plasma mass spectrometry (ICP-MS) (Barbaste et al., 2001; Munksgaard and Parry, 1998), and electrothermal atomic absorption spectrometry (ETAAS) (López-García et al., 2013; Yang et al., 2011) can be applied to determine lead trace levels. These techniques are expensive and more difficult to operate when compared to flame atomic absorption spectrometry (FAAS) (Gürkan et al., 2013; Lemos et al., 2010). The determination of lead is often an arduous task due to low concentration of the analyte, and matrix effects of the sample. Special techniques for the pre-treatment of samples, such as liquid–liquid extraction (LLE) (Comitre and Reis, 2005), solid-phase extraction (Q. He et al., 2013; Salarian et al., 2014; Siyal et al., 2014), cloud point extraction (CPE) (Shah et al., 2011), microwave oven (Gupta and Bertrand, 1995), wet digestion (Tinggi et al., 1992), low temperature ashing (Anderson, 1991) are required.

The multicommutated flow analysis (MCFA) system, when compared with the flow injection analysis (FIA) system, provides the advantages of speed, simplicity, flexibility, and versatility (Morales-Rubio et al., 2009; Pistón and Knochen, 2012; Melchert et al., 2012). Therefore, multicommutated flow systems have increased the analytical potential of flow analysis in applications employing solid-phase extraction (Germiniano et al., 2014; Maya et al., 2009; González et al., 2009) and pre-concentration (Dos Santos et al., 2011, 2014; Miranda et al., 2002). These procedures may increase the sensitivity and precision of the FAAS technique.

Milk is one of the foods most widely consumed in the world, mainly because it is considered as an excellent source of proteins, lipids and carbohydrates, minerals and vitamins. The presence of heavy metals, such as lead, in milk samples has been reported around the world (Saleh et al., 1996; Koyashiki et al., 2010; Rahimi, 2013). Aiming to develop a novel selective adsorbent for pre-concentration and determination of Pb(II) in milk samples, the present work reports on the synthesis, characterization and application of a new functionalized silica with 3,6-dithia-1,8-octanediol (Si-DIO). The matrix was characterized by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and nuclear magnetic resonance (NMR) of  $^{13}\text{C}$  and  $^{29}\text{Si}$ . The flow system based on a multicommutation approach, with FAAS detection, was developed in order to pre-concentrate and determine the presence of Pb(II) on-line.

## 2. Materials and methods

### 2.1. Reagents and solutions

All reagents used were analytical-grade chemical solutions prepared with deionized water (resistance  $<18.2\text{ M}\Omega\text{ cm}^{-1}$ ).

Pb(II) solutions were prepared by diluting the standard solutions of  $1004\text{ mg L}^{-1}$  (99.9% purity, SpecSol<sup>®</sup>). The solutions obtained had a concentration range from 5.0 to  $20,000.0\text{ }\mu\text{g L}^{-1}$ . Buffer solutions were used to control pH: hydrochloric acid–KCl (pH 2–3), sodium acetate–acetic acid (pH 4–5), sodium phosphate monobasic–dibasic sodium phosphate (pH 6–8), and sodium carbonate–sodium bicarbonate (pH 9–11). Hydrochloric and nitric acid concentrates were used to study the eluent with volume variations necessary to obtain the following solutions: 0.1, 0.5, 1.0, 1.5, 2.0 and  $2.5\text{ mol L}^{-1}$ .

The reagents used in the synthesis of the functionalized silica were 3,6-dithia-1,8-octanediol (DIO, 97%, Sigma–Aldrich), tetraethylorthosilicate (TEOS, 98%, Sigma–Aldrich), 1,4-dioxane (Vetec), ethanol (Vetec) and metallic sodium (Sigma–Aldrich).

### 2.2. Apparatus

The infrared spectra were obtained with a KBr tablet using a Varian<sup>®</sup> 640-IR model, FTIR spectrophotometer in the  $4000\text{--}400\text{ cm}^{-1}$  range with 32 scans, with a spectral resolution of  $8\text{ cm}^{-1}$ . Thermogravimetric curves were obtained using a TGA 50/50H Shimadzu under  $\text{N}_2$  atmosphere and a heating rate of  $0.167\text{ }^\circ\text{C s}^{-1}$ , at a flow of  $0.83\text{ cm}^3\text{ s}^{-1}$ , varying from 30 to  $700\text{ }^\circ\text{C}$ .

The NMR spectra were obtained using Bruker AC 300/P equipment at room temperature, at frequencies of 75.58 MHz to  $^{13}\text{C}$  and 59.62 MHz to  $^{29}\text{Si}$ , in the solid state (magic angle spinning – MAS). The scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) were obtained using a Quanta 200 FEG, FEI model.

The pre-concentration on-line experiments were coupled to a FAAS. The flow system was composed of six solenoid valves, three-way (161T031-NResearch), coils and transmission lines of polyethylene tube (0.8 mm diameter) and a homemade acrylic cylindrical column (4 mm i.d., 40 mm length) with two Teflon<sup>®</sup> barbed fitting connectors on the ends. Solutions were pumped employing a peristaltic pump (Gilson Minipuls 3, Villiers-le Bel, France) with Tygon tubing. The absorption measurements were made using a flame atomic absorption spectrometer (model AA240FS, Varian Inc., Palo Alto, CA, USA), equipped with a hollow cathode lamp of lead and a deuterium lamp for background correction. The hollow cathode lamp of lead was operated at 10 mA, with the wavelength fixed at 217.0 nm.

The solenoid valve was controlled by microcomputer (Intel Pentium dual core) equipped with a homemade electronic interface based on a ULN2803A integrated circuit with 12 V regulated power. This interface was coupled to the microcomputer in the LPT1 port (Line Printer Terminal) as described in reference Lavorante et al. (2005). The software used for control of the solenoid valves in the multicommutated flow system was written in LabVIEW 8.5<sup>®</sup>.

A microwave digester manufactured by CEM Corporation (Matthews, NC, USA) model MarsEXpress was used to process the milk sample digestion.

### 2.3. Synthesis of functionalized silica with 3,6-dithia-1,8-octanediol

The functionalized silica was obtained by a homogeneous route, employing sodium methoxide as the basic catalyst mixed in a 100 mL two-necked round bottom flask, equipped with a distillation bridge, 13.5 mmol of tetraethyl orthosilicate (TEOS), 13.5 mmol of 3,6-dithia-1,8-octanediol and  $0.435\text{ mol L}^{-1}$  of sodium methoxide solution, using 1,4-dioxane as the solvent (Fig. 1). The sodium methoxide had been prepared previously with a mixture of 50 mg of metallic sodium in methanol, under continuous stirring. The reaction was kept for 4 h at  $120\text{ }^\circ\text{C}$  to remove the ethanol produced from the reaction system. The product was washed (three times) with 1,4-dioxane and ethanol, and dried for 2 h at  $80\text{ }^\circ\text{C}$ .

### 2.4. Preparation of the minicolumn

In the acrylic minicolumn, 100 mg of functionalized silica and polyester screen were added to each end, in order to prevent leaching of the material. After, the minicolumn was packed, it was washed using the system flow with a solution  $0.5\text{ mol L}^{-1}$  of  $\text{HNO}_3$  and with deionized water, through of the switching on/off the  $V_3$  and  $V_4$  valves, respectively. Then, the  $V_2$  valve was switched on/off for inserting the buffer solutions, in order adjust the pH.

### 2.5. On-line pre-concentration procedure coupled with FAAS

The diagram of the multicommutation flow system for pre-concentration and determination of Pb(II) is shown in Fig. 2. The parameters of FAAS and the switching sequence of the valves for

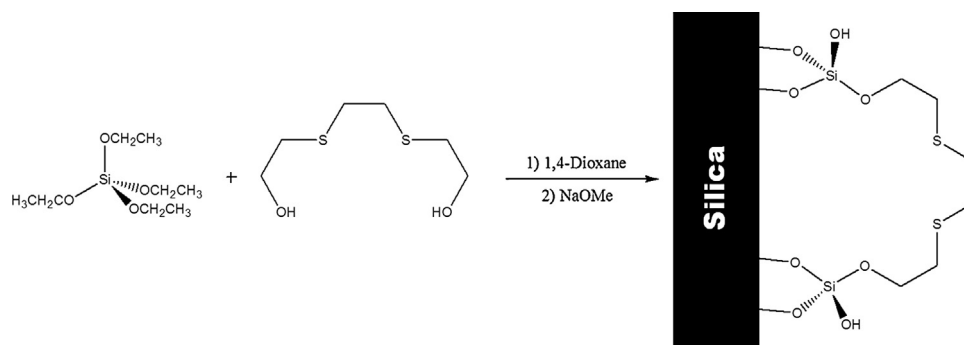


Fig. 1. Reaction scheme of the Si-DIO formation.

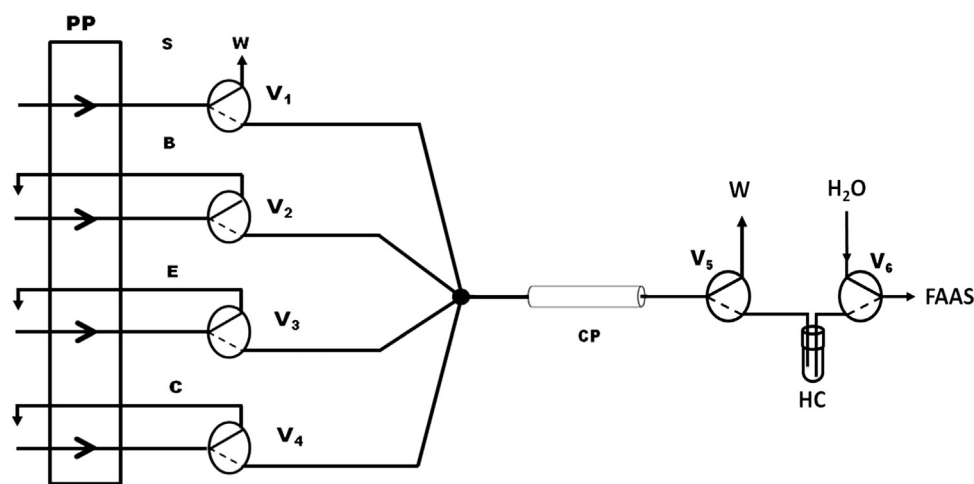


Fig. 2. Diagram of the multicommutated flow system for Pb(II) determination. PP = peristaltic pump; S = sample  $2.2 \text{ mL min}^{-1}$ ; B = buffer  $2.2 \text{ mL min}^{-1}$ ; E = eluent  $0.50 \text{ mL min}^{-1}$ ; C = carrier solution; CP = minicolumn of pre-concentration packed with silica modified (40 mm length  $\times$  4 mm diameter);  $V_1, V_2, V_3, V_4, V_5, V_6$  = three way solenoid valves; HC = holding chamber; FAAS = flame atomic absorption spectrometry W = waste. Arrows indicate the points of actuation of the peristaltic pump. Continuous line in solenoid valves indicates the flow direction in switch OFF position. Discontinuous line in solenoid valves indicates the flow in ON position.

pre-concentration and determination of Pb(II) are summarized in Table 1. Initially, the sample, buffer, eluent and carrier solutions were inserted in the flow system by the sequential switching on/off of the  $V_1$ – $V_4$  valves, respectively. After this, in the sampling step, valves  $V_1$ , and  $V_2$  were switched on/off sequentially, allowing the mix of slug samples and buffer solution, using the tandem procedure (Rocha et al., 2002). Then the  $V_3$  and  $V_5$  valves were switched on simultaneously, to perform the elution procedure with  $0.5 \text{ mol L}^{-1}$  of  $\text{HNO}_3$  solution and the eluate transported to a holding chamber (HC) of 1.6 mL. After this, the eluate was aspirated by FAAS through of the switched of the  $V_6$  valve. After elution, the minicolumn was washed with deionized water ( $V_4$  and  $V_5$  valves switched on), followed of the switched  $V_6$  valve and a new pre-concentration procedure was started as described in Table 1.

## 2.6. Sample preparation

Milk samples were purchased from local supermarkets. The decomposition of the milk samples was assisted by microwave according to a slightly modified procedure (Santos et al., 2005) and performed in triplicate. 1.0 mL of the milk sample and 1.0 mL of the concentrated  $\text{HNO}_3$  were poured into in a Teflon-PFA<sup>®</sup> and heated in the microwave. The details of programming the digestion procedure are described in Table 2. After the digestion procedure, the samples were neutralized ( $\text{pH} = 7.0$ ) with  $5 \text{ mol L}^{-1}$  of the

Table 1

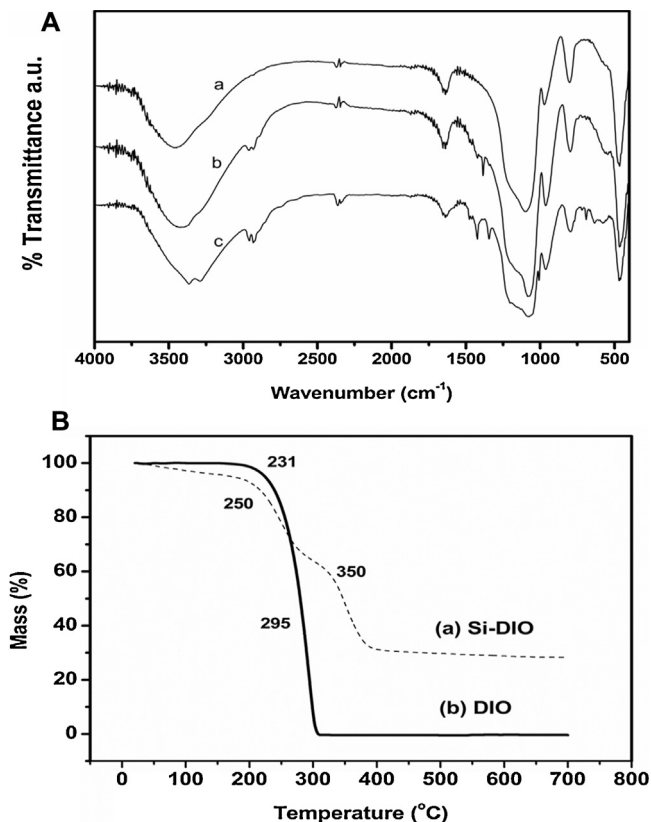
Operational sequence of the multicommutation flow system, for pre-concentration and determination of Pb(II) ions.

Flame atomic absorption spectrometry parameters									
Wavelength (nm)	217.0								
Lamp electric current (mA)	10.0								
Slit width (nm)	1.0								
Air gas flow ratio	13.5								
Acetylene gas flow ratio	2.0								
Background deuterium	ON								
Operational sequence of multicommutated flow system									
Step	$V_1$	$V_2$	$V_3$	$V_4$	$V_5$	$V_6$	Time (s)	Cycles	Comments
Flow lines filling	1 <sup>*</sup>	0 <sup>*</sup>	0	0	0	0	5	1	Column washing and conditioning
	0	1	0	0	0	0	5		
	0	0	1	0	0	0	5		
	0	0	0	1	0	0	5		
Sampling	1	0	0	0	0	0	8	180	Sample loading
	0	1	0	0	0	0	2		
Elution	0	0	1	0	1	0	60	1	Pushing eluent/ $\text{HNO}_3$
Detection	0	0	0	0	0	1	21	1	
Washing	0	0	0	1	1	0	60	1	Pushing Carrier/water
	0	0	0	0	0	1	21		

\* 0 and 1 represent that the solenoid valves are switched OFF and ON.

**Table 2**  
Parameters employed in the process of decomposition of milk samples.

Step	Power		Ramp		Hold
	Watts	%	Temperature (°C)	Minutes	Minutes
1	800	100	25 → 110	10:00	00:00
2	1600	100	110 → 170	10:00	10:00
3	Off	Off	170 → 40	15:00	00:00



**Fig. 3.** (A) FTIR spectra of silica (line a), Si-DIO after (line b) and before (line c) adsorption of Pb(II) ions; (B) TG curve of Si-DIO straight line and DIO dash dot line respe.

NaOH solution, transferred into a 25 mL volumetric flask, and the volume completed with deionized water. The blank samples were prepared using the same procedure. Finally, all solutions were stored in polyethylene bottles at 4 °C.

### 3. Results and discussion

#### 3.1. Characterization of the functionalized silica (Si-DIO)

The functionalized silica was solid white, with amorphous characteristics and low hygroscopicity. The infrared spectra of silica, Si-DIO before and after Pb(II) adsorption are presented in Fig. 3A.

The infrared spectra of Si-DIO exhibits the following vibration (stretching) modes: C–O–C (1120 cm<sup>-1</sup>), Si–O–C (1100 cm<sup>-1</sup>), Si–O–Si (1070 cm<sup>-1</sup>), CH<sub>2</sub> (2921 cm<sup>-1</sup>) and C–S (690 cm<sup>-1</sup>) suggesting that DIO was bonded in the silica. When Si-DIO spectra is recorded before and after Pb(II) adsorption, the presence of a new band is observed at 720 cm<sup>-1</sup> referring to the coordinated C–S group, suggesting that the interaction of the Si-DIO and Pb(II) ions is not purely physical.

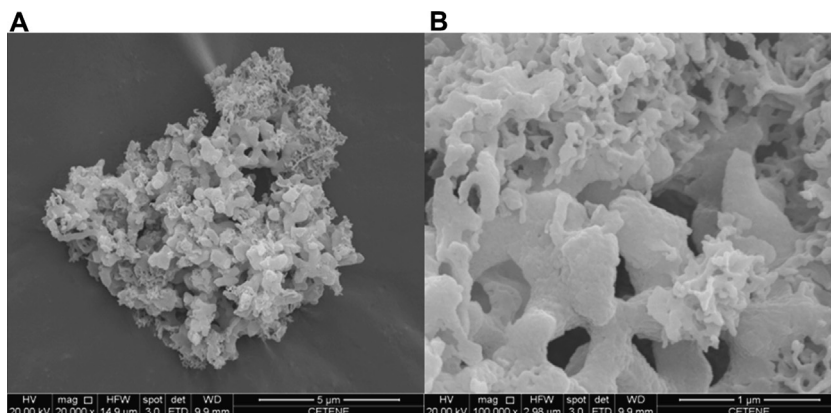
The TG curves of the DIO and Si-DIO are shown in Fig. 3B. An analysis of the TG curve of DIO indicates only one thermal event associated to its complete burning, at the on-set temperature of 231 °C. The TG curve of Si-DIO shows two thermal events up to 500 °C. The second event starting at 350 °C, suggesting that the DIO compound is bonded covalently to the silica. This event corresponds to a weight loss of 30.2%. The scanning electron microscopy (SEM) of the Si-DIO is presented in Fig. 4(A) at 20,000× and (B) at 100,000×.

The Si-DIO material showed homogeneous morphology and porosity with the presence of clusters. The chemical composition of Si-DIO was determined by energy dispersive spectrometer (EDS). The EDS spectra were used to identify the existence of a particular element in the silica material obtained. Si-DIO data showed peaks for C, O, S and Si, corroborating with the expected results for the synthesized material, in this case silica functionalized with 3,6-dithia-1,8-octanediol. The NMR spectrum of <sup>29</sup>Si presents silicon units of the Q4 and Q3 types, at 110.7 and 99.7 ppm, respectively. In the case of NMR spectrum of <sup>13</sup>C, signals were exhibited at 29.56 and 30.45 ppm, referring to the CH<sub>2</sub> groups; and 63.09 ppm, referring to the CH<sub>2</sub>–O–Si groups. These results are compatible with the formation of the silacrown proposed structure (Fig. 1). NMR spectra are not shown in the text.

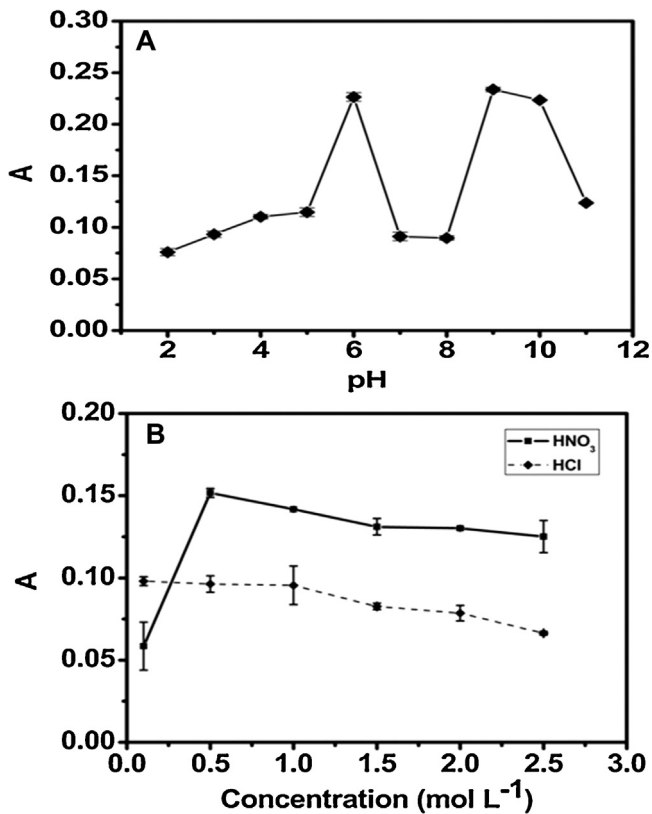
#### 3.2. System optimization

##### 3.2.1. pH effect

The effect of pH in the study of metallic ions extraction in solid phase is an essential parameter, mainly for the quantitative recoveries of the analytes (Tarley et al., 2005). In order to optimize this test variable, the pH influence on the adsorption process of Pb(II) was studied in the 2–11 range, with all solutions maintained



**Fig. 4.** Scanning electron microscope on a scale bar of 5 μm (A) and 1 μm (B).



**Fig. 5.** (A) The pH effect on the analytical signal influence of the eluent nature for lead rate flow of 2.2 mL min<sup>-1</sup>, employing as eluent HNO<sub>3</sub> 0.5 mol L<sup>-1</sup> of concentration and rate flow of 1.4 mL min<sup>-1</sup> and concentration on the analytical signal for 1.0 mg L<sup>-1</sup> of Pb(II) flow rate 1.4 mL min<sup>-1</sup> and pH 9.0. (B) Effect of the nature of the eluent.

at a Pb(II) solution flow rate of 1.4 mL min<sup>-1</sup> and 1.0 mg L<sup>-1</sup>. Fig 5A shows the pH effect on the Pb(II) adsorption. Analyzing the pH study data, was observed a higher absorbance to pH 9.0 and 6.0, the latter being due to decrease of concentration hydrogen ions which competes with Pb(II) ions during the adsorption process (Dadfarinia et al., 2006; Liu and Liang, 2008; Wang et al., 2012).

At pH 9.0 an absorption increase could be observed, probably due the formation of a cationic species such as PbOH<sup>+</sup>, [Pb<sub>3</sub>(OH)<sub>4</sub>]<sup>2+</sup> and [Pb<sub>6</sub>(OH)<sub>8</sub>]<sup>4+</sup> (Depci et al., 2012; Xue et al., 2009), that interacts strongly with adsorbent material. Considering these results, pH 9.0 was selected using a sodium bicarbonate/sodium carbonate buffer.

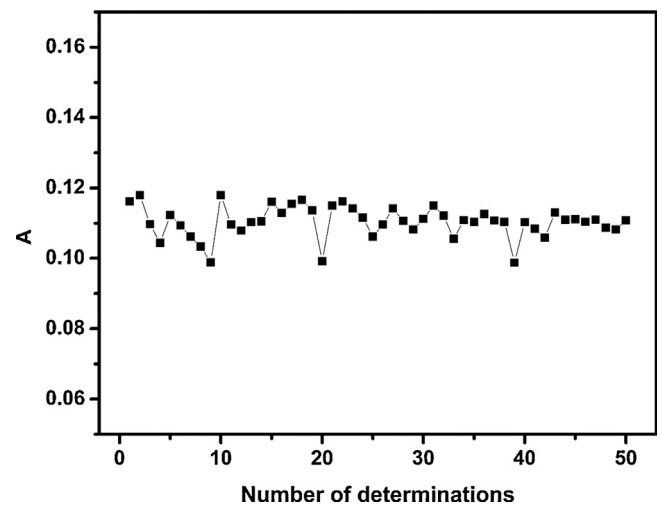
### 3.2.2. Eluent solution: effect of nature, concentration, volume and flow rate

As shown in Fig. 5A, the adsorption of Pb(II) decreases as the pH decreases. Because of this, hydrochloric and nitric acid were

**Table 3**

Optimized parameters for determination of lead in milk, employing in the flow multicommutated for the pre-concentration and determination of Pb(II) ions.

Parameters	Evaluated interval	Selected value
pH	2.0–11.0	9.0
Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub> buffer volume (mL)	4.2–16.8	8.4
Eluent HCl and HNO <sub>3</sub> /concentration HNO <sub>3</sub> (mol L <sup>-1</sup> )	0.1–2.5	HNO <sub>3</sub> /0.50
HNO <sub>3</sub> flow ratio (mL min <sup>-1</sup> )	1.4–2.4	1.4
HNO <sub>3</sub> volume (mL)	1.4–2.4	1.4
Sample flow ratio (mL min <sup>-1</sup> )	0.45–2.2	2.2
Sample volume (mL)	4–64	52.8



**Fig. 6.** Stability study of the adsorbent, number of sampling cycles with analytical signal for 1.0 mg L<sup>-1</sup> of lead and HNO<sub>3</sub> 0.5 mol L<sup>-1</sup> as eluent, rate flow 1.4 mL min<sup>-1</sup> for both and pH 9.0.

selected to study the nature and concentration of the eluent. For this purpose, the concentration of acids used varied between 0.1 and 2.5 mol L<sup>-1</sup> (Fig. 5B). In order to get the most efficiency from the eluting agent, the pH was maintained at 9.0 and the flow rate at 1.4 mL min<sup>-1</sup>. The best efficiency was obtained with a 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> solution (Fig. 5B).

The volume study of the eluent was accomplished by varying the volume between 1.4 and 2.4 mL at increments of 0.2 mL; using a 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> solution. This study was initiated with a value of 1.4 mL, as this was the volume of sample necessary to measure using the FAAS. The eluent volume needed for complete desorption of the Pb(II) ions was 1.4 mL, and therefore was selected for other studies. The flow rate study of the Pb(II) ions was accomplished by varying the HNO<sub>3</sub> solution by 0.1, 0.2, 0.45, 0.85, 1.4, and 2.2 mL min<sup>-1</sup>. The flow rate that presented the strongest analytical signal was obtained at 1.4 mL min<sup>-1</sup>.

### 3.2.3. Samples: effect of flow rate and volume

The physical and chemical parameters were studied to determine the maximum analytical signal. The flow rate of the sample in the adsorption process of Pb(II) ions determines the contact time of the sample solution with the solid phase adsorbent. Flow rate of Pb(II) standard solutions was varied within the range of 0.45–2.2 mL min<sup>-1</sup>. The highest analytical signal was at 0.45 mL min<sup>-1</sup>, due to the longer contact time between the adsorbate and adsorbent. However, the procedure time and limit

**Table 4**

Recovery of Pb(II) in the milk samples.

Sample	Pb(II) amount (μg L <sup>-1</sup> )		Recovery (%)
	Add	Found	
1	0.0	n.d. <sup>a</sup>	–
	40.0	38.2	95.5
2	0.0	n.d.	–
	40.0	40.3	100.7
3	0.0	n.d.	–
	40.0	41.0	102.5
4	0.0	n.d.	–
	40.0	38.1	95.2
5	0.0	n.d.	–
	40.0	36.3	90.7
6	0.0	n.d.	–
	40.0	38.7	96.7

<sup>a</sup> Not detected.

**Table 5**

Analytical features of methodologies that employ solid phase extraction for Pb(II) determination by FAAS.

Solid-phase	Linear range ( $\mu\text{g L}^{-1}$ )	Detection limit ( $\mu\text{g L}^{-1}$ )	Enrichment factor	Sample volume (mL)	Column reusability	Pre-concentration modality	Reference
Si-DIO	5.0–20,000.0	1.00	28	52.8	50	On-line	This work
Ionic liquid-modified silica	100–750	0.7	N.A.	150.0	10	Off-line	Ayata et al. (2011)
Si-DHPM <sup>a</sup>	0.1–0.3	0.53	N.A.	750.0	10	Off-line	Sabermahani et al. (2013)
Si-TU <sup>b</sup>	100.0–600.0	0.57	N.A.	300.0	60	Off-line	Mendil (2012)
Si-DHAQ <sup>c</sup>	1000.0–15,000.0	0.45	N.A.	1000.0	15	Off-line	Goswami and Singh (2002)
Si-GASG <sup>d</sup>	1000.0–5000.0	0.58	N.A.	2000.0	10	Off-line	Xie et al. (2008)
Mesoporous silica with MTTZ <sup>e</sup>	400.0–6010.0	0.46	N.A.	1000.0	3	Off-line	Pérez-Quintanilla et al. (2009)
Silica with zirconium (IV) phosphate	N.A.	6.10	30	400.0	5	Off-line	Matoso et al. (2003)

N.A., not available.

<sup>a</sup> Si-DHPM, silica gel modified with allyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.<sup>b</sup> Si-TU, silica gel modified with thiourea.<sup>c</sup> Si-DHAQ, silica gel modified with 1,8-dihydroxyanthraquinone.<sup>d</sup> Si-GASG, silica gel modified with gallic acid.<sup>e</sup> 5-Mercapto-1-methyltetrazol.

detection are important because the adsorption increase occurs when the standard solution volume is kept constant (17.6 mL). The flow rate of 2.2 and 0.45 mL min<sup>-1</sup> showed similar enrichment factors, and due to this, was selected the flow of 2.2 mL min<sup>-1</sup>. Sample volume investigation is very important for analysis and quantification of low concentrations of analytes. For this, the Pb(II) solutions (1.0 mg L<sup>-1</sup>) were varied between 8.8 and 176 mL, with changes in the number of sampling cycles controlled directly by the software. In this study, volumes above 70.4 mL generated a constant analytical response. Since the volume used in this study was 52.8 mL, it was equivalent to 180 sampling cycles. This volume was sufficient to reach the detection limit required for determining Pb(II) ions in milk samples. The data of the parameters of optimization of the pre-concentration system are summarized in Table 3.

### 3.2.4. Reusability and capacity of the adsorbent

Reusability is a key parameter to evaluate the efficiency of an adsorbent. As can be seen in Fig. 6, the stability and regeneration of Si-DIO was investigated on-line through several repetitions of the process of pre-concentration, always regenerated with 1.4 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> (desorption) and 1.1 mL of deionized water, for a total of 90 seconds. The modified silica (Si-DIO) was reused 50 times, and significant differences of absorbance were not found.

For the estimation of the modified silica adsorption capacity was performed the kinetic study to determine the minimum time required to obtain the maximum adsorption capacity of Si-DIO. Thus, the saturation time between 1 and 40 min at 25 °C was studied. The saturation time of the adsorbent was of 5 min, indicating a rapid extraction. The adsorption capacity was measured by mixing 50 mL of 0.5 mg L<sup>-1</sup> solution of Pb(II), pH 9.0 with 100 mg of the adsorbent for 2 h under constant stirring. The mixture was filtered and determined by atomic absorption spectrometry. The modified silica (Si-DIO) was reused 50 times and did not present significant differences in absorption (3.8% error). A maximum capacity of 2.22 mg g<sup>-1</sup> (milligrams of lead per gram of Si-DIO) adsorption of functionalized silica was established.

After optimization of the conditions, we achieved at the equation  $Y = (0.5394 \pm 0.0109) B + (0.0056 \pm 0.0004)$ , where  $B$  is the concentration of Pb(II) in solutions (mg L<sup>-1</sup>), with  $r = 0.9939$  for the linear response from 5.0 to 20,000.0  $\mu\text{g L}^{-1}$ . The relative standard deviation of 3.8% ( $n = 50$ ) using a solution of 1.0 mg L<sup>-1</sup> of Pb(II) was estimated. The value of the experimental limit detection (LOD) of 1.0  $\mu\text{g L}^{-1}$  was found. The enrichment factor at 28 was calculated through of the ratio between the slopes of the calibration graphs with and without pre-concentration. The time of process pre-concentration was about 30 min.

The proposal method was applied to determine Pb(II) in milk samples, and the recovery study was realized with six samples through addition/recovery of the Pb(II) standard solutions, as shown in Table 4. In milk samples, lead concentrations were below detection limit even using the proposed pre-concentration system. This fact demonstrates that the samples tested did not contain lead. Agreement was obtained between the added and established content of the analytes. The results of the recoveries were found in the range between 90.7 and 102.5%.

Table 5 represents some other methods of pre-concentration, where it can be noted that the proposed method has advantages over the others, as well as using a new material with easy synthesis, presenting an enrichment factor with low sample consumption and with up to 50 times reusability with no substantial change in the analytical signal. The pre-concentration procedure is performed in a multicommutated automated flow system, which makes the method easy to operate, with excellent reproducibility and repeatability.

## 4. Conclusion

Functionalized silica was synthesized (through a sol-gel process) and characterized. The immobilization of the DIO on the silica surface offered several advantages, such as higher thermal stability and possibility of chemical interaction (bond) through the thiol-groups. The Si-DIO was applied as adsorbent for pre-concentration and quantitative separation of lead on-line for later quantification/determination by absorption by atomic spectrometry flame. The proposed method is an alternative procedure to the Graphite Furnace Atomic Absorption Spectrometry method for Pb(II) determination at ppb level ( $\mu\text{g L}^{-1}$ ).

The multicommutated flow system promoted a quantitative pre-concentration procedure, enabling satisfactory values for sensitivity, precision and accuracy in real samples. The packaging of the minicolumn used in the on-line proposed procedure did not show extra pressure can be reused up to at least 50 process of adsorption–elution without a decrease in performance. Other main benefits of this system are the low influence of interference ions, increase of sensitivity of the FAAS method, low cost and simplicity.

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