Journal of Food Composition and Analysis xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Original Research Article

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

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

[a] Departamento de Química, Universidade Federal Rural de Pernambuco, Rua Dom Manuel de Medeiros, S/N, Dois Irmão, 52171-900 Recife, PE, Brazil
[b] Departamento de Química Fundamental, Universidade Federal de Pernambuco, Av. Prof. Luiz Freire, S/N, Cidade Universitária, 50740-540 Recife, PE, Brazil
[c] Centro de Tecnologias Estratégicas do Nordeste, Av. Prof. Luiz Freire, 1, Cidade Universitária, CEP: 50740-540 Recife, PE, Brazil

ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 15 December 2014
Accepted 28 December 2014
Available online xxx

Keywords:
Lead
Heavy metals in food chain
Food analysis
Food composition
Functionalized silica
Solid phase extraction
Multicommutation
Flame atomic absorption spectrometry
Food safety methods

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 ^{13}C and ^{29}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^{-1} Pb(II) at pH 9.0 and HNO_3 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^{-1}; a linear coefficient where $r = 0.9939$ and $n = 7$; a detection limit estimated at 0.001 mg L^{-1} and a relative standard deviation of 3.8% ($n = 30$). 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%.

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^{-1} (equivalent to 3.5 μg kg^{-1} 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 compared

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

http://dx.doi.org/10.1016/j.jfca.2014.12.025
0889-1575/© 2015 Published by Elsevier Inc.

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; Gonzáles 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 (I 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}C and ^{29}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 MΩ cm^{-1}).

Pb(II) solutions were prepared by diluting the standard solutions of 1004 mg L^{-1} (99.9% purity, SpecSol®). The solutions obtained had a concentration range from 5.0 to 20,000.0 μg 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 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® 640-IR model, FTIR spectrophotomer in the 4000–400 cm^{-1} range with 32 scans, with a spectral resolution of 8 cm^{-1}. Thermogravimetric curves were obtained using a TGA 50/50H Shimadzu under N_2 atmosphere and a heating rate of 0.167 °C s^{-1}, at a flow of 0.83 cm^3 s^{-1}, varying from 30 to 700 °C.

The NMR spectra were obtained using Bruker AC 300/P equipment at room temperature, at frequencies of 75.58 MHz to ^{13}C and 59.62 MHz to ^{29}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® 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 multicommuted flow system was written in LabVIEW 8.5®.

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 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 °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 °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 mol L^{-1} of 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

Please cite this article in press as: da Silva, P.A.B., et al., Synthesis and characterization of functionalized silica with 3,6-ditia-1,8-octanediol for the preconcentration and determination of lead in milk employing multicommuted flow system coupled to FAAS. J. Food Compos. Anal. (2015), http://dx.doi.org/10.1016/j.jfca.2014.12.025