Food Chemistry 127 (2011) 364–368

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

Pyridine-functionalized mesoporous silica as an adsorbent material for the determination of nickel and lead in vegetables grown in close proximity by electrothermal atomic adsorption spectroscopy

O. Sadeghi, N. Tavassoli, M.M. Amini *, H. Ebrahimzadeh, N. Daei

Department of Chemistry, Shahid Beheshti University, G.C., Tehran 1983963113, Iran

ARTICLE INFO

Article history:
Received 14 August 2010
Received in revised form 4 November 2010
Accepted 31 December 2010
Available online 8 January 2011

Keywords:
MCM-48
Nickel determination
Lead determination
ETAAS
Vegetable

ABSTRACT

A new, sensitive, and low cost solid-phase extraction method using pyridine-functionalized MCM-48 mesoporous silica for the extraction, pre-concentration, and electrothermal atomic absorption spectrometric determination of nickel and lead in food samples at ng mL^{-1} levels is described herein. The levels of nickel and lead in different types of vegetables grow in Shiraz–Iran and Rafsanjan–Iran were determined by electrothermal atomic absorption spectrometry. The use of two standard reference materials and also comparing the results to a standard reference procedure ensured the accuracy of this method. Factors, such as flow rate of extraction, and the type, pH, concentration, and volume of eluent, were appraised. The effect of various ions on recovery was also investigated. Detection limits of 0.11 and 0.14 ng mL^{-1} were obtained for lead and nickel, respectively.

1. Introduction

The toxicity and effect of trace heavy metals on human health and the environment has attracted considerable attention and concern in recent years. Heavy metals are categorised as environmentally toxic materials that can harm the natural environment at low concentrations, with an inherent toxicity, a tendency to accumulate in the food chain, and a particularly low decomposition rate. Nickel is a moderately toxic element compared to other transition metals that can lead to serious illness, including malignant tumours and nasopharynx, lung, and dermatological diseases (Jiang, Chang, Zheng, He, & Hu, 2006; Spears, 1984). However, nickel is an essential element for humans, other animals, and plants (Eskew, Welch, & Norwel, 1984; Wang & Hansen, 2000). The main sources of nickel in aquatic systems are industrial processes, atmospheric fall out, biological cycles, and the dissolution of rocks and soil. However, food and water are the only possible sources of nickel for humans. Therefore, the determination and monitoring of nickel in drinking water and foods are very important for public health. This detection has become most critical for people using water and vegetable grown in the vicinity of factories that process nickel.

Lead is another heavy metal that has attracted a considerable amount of interest among environmental scientists due to the cumulative toxicity and associated well-known health risk to mammals even at very low concentrations (Shamsipur, Raoufi, & Sharghi, 2000). Furthermore, lead is one of the most ubiquitous elements in the environment. As a result of its widespread industrial application, particularly as a fuel additive released into the biosphere in large quantities, lead has become recognised as a major health risk to mammals (Ryan et al., 2004). The primary sources of lead in humans and other animals include food, beverages, water, soil, and paint (Mahaffey, 1995). Therefore, the development of analytical methods that are rapid with low detection limits is necessary.

Several techniques have been used to determinate the levels of nickel or lead in foods. These include electrothermal atomic absorption spectrometry (ETAAS) (Jinlan & Lei, 1995; Tuezen, 2003), inductively coupled plasma mass spectroscopy (Lee, Muaroka, Oshima, & Motomizu, 2004), inductively coupled plasma optical emission spectroscopy (ICP-OES) (Bezerra, Santos, Lemosc, Korn, and Ferreira, 2007) and flame atomic absorption spectroscopy (FAAS) (Lemos, Gama, & Lima, 2006). Due to the high selectivity and sensitivity of ETAAS, this method is one of the most powerful and popular analytical tools for the determination of low concentrations of heavy metals present in environmental and biological samples. However, there are some disadvantages of ETAAS that include the high detection limit and chemical interference from both sample and matrix. The greatest challenge in the direct determination of trace levels by ETAAS is the low concentration of metal ions in samples. Additionally, a careful and time consuming cleanup stage is often required because waste water, river water, vegetable food, or most any other real sample contains high levels of non-toxic compounds that usually accompany analysis (Amin, 2009). Avoiding chemical

---

* Corresponding author. Tel.: +98 21 29903109; fax: +98 21 22431661.
E-mail address: m-pouramini@cc.sbu.ac.ir (M.M. Amini).

0308-8146/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2010.12.159

interference becomes a particularly difficult task in the analysis of complex matrices, such as wastewater, river water, food samples, and vegetables. In this context, other methods have been proposed and used for the pre-concentration and separation of trace elements according to the nature of the samples, analyte concentration, and the measurement technique, which may include co-precipitation (Sibel Saracoglu, Soylak, & Elci, 2003), ion exchange (Kong, Jia, and Zhou, 2007), and solid-phase extraction (SPE) (Tokalıoğlu & Gürbüz, 2010). SPE is most often used due to the advantages of this method including flexibility, low cost, attenuated consumption of solvent, simplicity, fast rate of analysis, ease of automation, and decreased environmental pollution. During the SPE process, analytes are transferred from the liquid phase to the active sites of the adjacent solid-phase and then to a liquid phase that is always water (Prasada Rao, Daniel, and Mary Gladis, 2004). Analyte and sorbent are varied until the optimal condition is achieved in the system. After sorption on the solid-phase, the analyte is removed with the proper eluent for further analysis. The choice of adsorbent is important in SPE to control various analytical parameters, such as selectivity, affinity, and capacity. Among the many types of adsorbent material used in SPE, functionalized mesoporous silica, such as MCM-48 mesoporous silica, has received great attention for the good mechanical and thermal stability coupled to the decreased susceptibility to swelling and shrinking of this material (Quintanilla, Sanchez, Hierro, Fajardo, and Sierra, 2007). In this report, pyridine-functionalized mesoporous silica, py-MCM-48, was prepared by refluxing of *N*-[3-(triethoxysilyl)propyl]isonicotinamide (TPI) with MCM-48. This new sorbent has a high sorption capacity for the solid-phase extraction of nickel and lead ions in environment samples. We describe herein the application of functionalized mesoporous silica for the determination of nickel and lead ions by electrothermal atomic absorption spectrometry "in vegetables grown in close proximity of Khoshk (Shiraz, Iran) and Sarcheshmeh (Rafsanjan, Iran) rivers."

2. Materials and methods

2.1. Instrumentation

Determination of nickel and lead concentration was performed with a Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer equipped with a pyrolytically-coated GFA-4A graphite furnace atomizer. Nickel and lead hollow cathode lamps (Hamamatsu photonics K.K., Japan) were employed as radiation sources. All analyses were performed under the conditions suggested by the manufacturer. The instrumental parameters for nickel and lead analysis were as follows: wavelength, 217.0 and 232.0 nm; lamp current, 7 and 7 mA; and argon purge gas, 1.5 and 1.5 L min^{-1}, respectively. The pH measurements were determined with a digital WTW Metrohm 827 Ion analyser (Switzerland) equipped with a combined glass-calomel electrode. A Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

The instrumental parameters for analysis were the following: drying temperature of 150 °C (ramp 60 s) for nickel and 150 °C (ramp 60 s) for lead; pyrolysis temperature of 1000 °C (hold 40 s) for nickel and 600 °C (hold 40 s) for lead; atomization temperature of 2400 °C (hold 4 s, gas stop) for nickel and 1300 °C (hold 3 s, gas stop) for lead; and cleaning temperature of 3000 °C (hold 2 s) for nickel and 2000 °C (hold 2 s) for lead.

2.2. Reagents

All reagents were purchased from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Standard solutions of nickel or lead ions were prepared daily by appropriate dilution of a 1000 μg L^{-1} stock solution of nickel or lead from Merck. All of the required solutions were prepared using deionized water from a Milli-Q (Millipore, Bedford, MA, USA) purification system. *N*-[3-(triethoxysilyl)propyl]isonicotinamide (TPI) (Hoogbomm, Garcia, and Otten, 2005), MCM-48 (Schumacher, Grun, and Unger, 1999) mesoporous silica was prepared as previously reported. MCM-48 was functionalized by TPI similarly to the general procedure used for functionalization of mesoprous silica by amine (Yoshitake, Yokoi, & Tatsumi, 2002). In a typical reaction, 1.0 g of MCM-48 was suspended in 50 ml toluene and the mixture was stirred for 1 h followed by addition of 2.0 g TPI and reflux for 2 h. The white-brownish solid was removed from the solvent by filtration, washed with toluene and chloroform, and dried at room temperature. Synthesis of MCM-48 and pyridine-functionalized materials were confirmed by IR spectroscopy, low-angle X-ray diffraction, and elemental analysis. Elemental analysis of py-MCM-48 sample yielded a pyridine concentration of 1.85 mmol g^{-1}. A schematic diagram of modified MCM-48 with pyridine is shown in Fig. 1.

2.3. Sample collection and preparation

Samples of cabbage, mint, lettuce, weed, rice, wheat, tomato, potato, corn, and apple were collected along the cultivated banks of the Khoshk river (Shiraz, Iran). Cultivated Rafsanjan samples are rare; therefore, some arbitrarily grown vegetables were used. The samples were collected from these growing areas over a period of four weeks during summer 2009. Water samples from the Khoshk (Shiraz, Iran) were also collected over a four-week period during the summer similar to the vegetable samples. All the samples were stored in polythene bags according to their type and brought to the laboratory for preparation and treatment. After washing the vegetables with distilled water, 10.0 g of each sample was ground, homogenised, and dried at 80 °C and triturated in a porcelain mortar. After fractionation of samples by sieving, sizes less than 20 μm were dissolve in 10 mL of 3 mol L^{-1} HNO_3 solution and diluted with distilled water to a final volume of 100 mL.

2.3.1. Dissolution of standard material leaves

A known quantity (0.40 g) of standard reference leaves (NIST 1571 (Orchard leaves) and NIST 1572 (Citrus leaves) were dried at 80 °C for 2 h. Afterwards, 0.50 g of the dry material was decomposed in a quartz vessel with 1 mL concentrated HCl and 4 mL HNO_3. Finally, deionized water was added to the digested samples to yield a total volume of 25 mL.

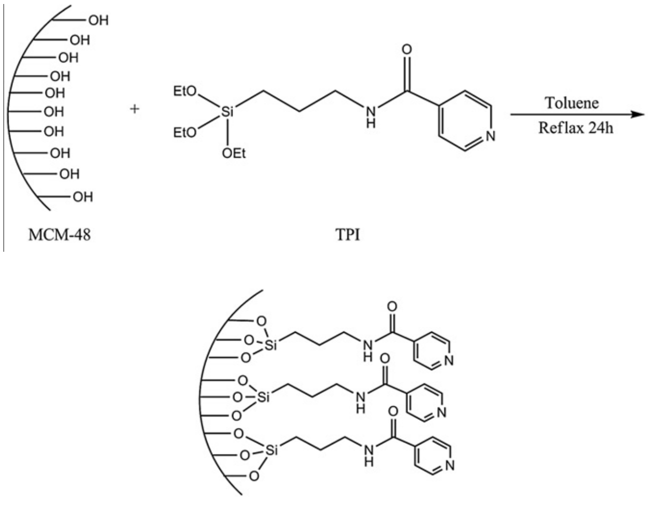

Fig. 1. A schematic model for modifying mesoporous MCM-48 with pyridine.