Spectrochimica Acta Part B 101 (2014) 15–20

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Analytical Note

# Multiwalled carbon nanotubes as a sorbent material for the solid phase extraction of lead from urine and subsequent determination by electrothermal atomic absorption spectrometry

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ARTICLE INFO

*Article history:*
Received 27 February 2014
Accepted 14 July 2014
Available online 23 July 2014

*Keywords:*
SPE
Carbon nanotubes
Lead
Urine
Electrothermal atomic absorption spectrometry

ABSTRACT

The determination of lead in urine is a way of monitoring the chemical exposure to this metal. In the present paper, a new method for the Pb determination by electrothermal atomic absorption spectrometry (ETAAS) in urine at low levels has been developed. Lead was separated from the undesirable urine matrix by means of a solid phase extraction (SPE) procedure. Oxidized multiwalled carbon nanotubes have been used as a sorbent material. Lead from urine was retained at pH 4.0 and was quantitatively eluted using a 0.7 M nitric acid solution and was subsequently measured by ETAAS. The effects of parameters that influence the adsorption–elution process (such as pH, eluent volume and concentration, sampling and elution flow rates) and the atomic spectrometry conditions have been studied by means of different factorial design strategies. Under the optimized conditions, the detection and quantification limits obtained were 0.08 and 0.26 μg Pb $L^{-1}$, respectively. The results demonstrate the absence of a urine matrix effect and this is the consequence of the SPE process carried out. Therefore, the developed method is useful for the analysis of Pb at low levels in real samples without the influence of other urine components. The proposed method was applied to the determination of lead in urine samples of unexposed healthy people and satisfactory results were obtained (in the range 3.64–22.9 μg Pb $L^{-1}$).

## 1. Introduction

Lead is a toxic heavy metal that does not have any known positive physiological role in the human body. Exposure to lead causes a variety of diseases and undesired health consequences. An overview of the adverse effects that this metal has on the human organism is given in the review by Needleman [1]. The main sources of Pb exposure include smoking, contaminated air (mainly from tetraethyl lead used as a motor fuel additive), water, soil, food, and consumer products [2]. Occupational exposure in the workplace is the most common cause of lead poisoning in adults, particularly in the smelting, scrapping and printing industries, battery manufacture, pigment production, chemical and plastics industries, mining and metal work [3]. Since the lead level in urine reflects the amount of the element that has been recently absorbed, the determination of Pb in urine is useful for assessing occupational and environmental exposure [4]. Monitoring trace elements in urine is a difficult task due to the complexity of the matrix and the low concentration of analyte [5]. Therefore, the determination of Pb in urine requires a pretreatment step as well as sensitive instrumental techniques such as inductively coupled plasma-mass spectrometry (ICP-MS) and electrothermal atomization atomic absorption spectrometry (ETAAS) [6,7].

ETAAS has been used for the determination of normal concentrations of this element in urine. However, the sample matrix represents the main drawback for the measurements due to the considerable amount of numerous components in urine that might cause incomplete atomization, volatilization of lead, high background levels and the formation of carbonaceous residues in the atomizer [8]. Therefore, stabilized temperature-platform furnace (STPF) conditions, different matrix modifiers and Zeeman background correction are essential to overcome these problems [9–11]. However, these strategies are not enough to suppress all of the problems in urine measurements and it may be necessary to remove the sample matrix [12]. For these reasons, prior to measurement, different techniques for the separation of lead from urine have been applied. The most widely used technique for this objective was solid-phase extraction (SPE) [13–15]. SPE has proven to be one of the suitable methods because of the following advantages: high enrichment factor, good recovery, rapidity, small quantities of organic solvents, possibility of automation of the whole process and the availability of a wide variety of sorbents.

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http://dx.doi.org/10.1016/j.sab.2014.07.005
0584-8547/

Since the discovery of carbon nanotubes (CNTs) in 1991 by Ijima [16], it became clear that they might be an excellent material for SPE because of their high surface area and inner volume, stability, mechanical strength and the possibility of establishing π–π interactions. Therefore, since 1995 the works using diverse types of CNTs as SPE sorbents for metal preconcentration purposes have increased significantly [17,18]. In the case of Pb, different SPE procedures involving as-grown and oxidized CNTs have been proposed for separating and preconcentrating the metal, either directly in the form of Pb(II) ions [19–21], or as Pb-chelates [22,23]. In addition, other methods employ functionalized CNTs as SPE sorbents [24–26]. In all cases, after extraction, Pb was measured by different atomic spectrometric techniques with adequate results. However, the main focus of these methods was directed to a single matrix such as diverse types of waters.

The aim of the present study was to develop a SPE–ETAAS method for the determination of Pb in urine using multiwalled carbon nanotubes (MWCNTs) as SPE-sorbent. The SPE procedure achieved the elimination of the urine matrix and avoided the need for other sample pretreatment. Furthermore, Pb levels were determined with appropriate analytical figures of merit. The capability of the developed method for monitoring Pb exposure was demonstrated by measuring real urine samples.

## 2. Material and methods

### 2.1. Apparatus and statistical software

A Zeeman correction Varian-SpectrAA-600 atomic absorption spectrometer (Varian Inc., Palo Alto, CA, USA) equipped with a Varian GTA-100 electrothermal atomizer linked to an automatic sample dispenser was used for this work. Measurements were performed using a Pb Varian hollow cathode lamp operating at 283.3 nm with a current intensity of 10 mA. The bandwidth employed was 1.0 nm in all cases. Argon was used as the inert gas at a flow rate of 300 mL $min^{-1}$. Pyrolytic graphite-coated atomization tubes with a pre-inserted Omega Platform were used (Schunk Ibérica S.A., Madrid, Spain). A Gilson Minipuls-3 peristaltic pump (Gilson Inc., Middleton, WI, USA) equipped with Tygon pump tubing of 1.42 mm i.d. (Ismatec, Wertheim, Germany) was used to propel both the sample and reagents. Polytetrafluoroethylene (PTFE) connecting tubing of 0.5 mm i.d. and various end-fittings and connectors (Omnifit-Diba Industries Ltd, Cambridge, UK) were employed. Sample pH measurements were performed by using a HI221 Calibration Check Microprocessor pH meter (Hanna Instruments S.L., Spain).

Experimental designs as well as Pareto and surface contour plots for the optimization of the developed method were carried out using Statgraphics Centurion XVI ver. 16.1.15 (Rockville, MD, USA).

### 2.2. Reagents

Untreated multiwalled CNTs (purity > 95%, 20–30 nm o.d. and ~30 μm length) prepared by Chemical Vapor Deposition (CVD) of acetylene in hydrogen flow were supplied by Chengdu Organic Chemicals Co. Ltd. (Chengdu, China).

A standard lead stock solution (1.0 g $L^{-1}$) was obtained from Panreac (Barcelona, Spain) and diluted as necessary to obtain the working standard solutions. Ammonium dihydrogenphosphate was obtained from Fluka (Buchs, Switzerland). The pH adjustment of urine samples was carried out using different nitric acid solutions obtained from ultra-pure $HNO_3$ (Merck, Darmstadt, Germany). All materials were washed with 10% nitric acid (v/v) for a period of 24 h, rinsed with copious amounts of pure water and shaken dry before being used. The cleaning solution employed to wash the sampling capillary contained 0.7% (w/v) $HNO_3$ and 0.2% (v/v) Triton X-100 (Sigma-Aldrich, St. Louis, MO, USA).

### 2.3. MWCNT pretreatment and microcolumn preparation

The oxidation of MWCNT introduces hydroxyl, carbonyl and carboxyl groups on the nanotube surface and this enhances the solubility of the material and produces bonded surface oxygen-containing radicals that have the ability to retain a variety of metal ions at the appropriate pH [18]. In the present work, MWCNTs were oxidized by a microwave-assisted procedure employing the mixture $H_2SO_4/KMnO_4$ as oxidant. The procedure has been described in detail in a previous work [27]. The surface functionalization obtained by oxidation was quantitatively determined using Boehm's titration method [28]. A suitable total acidity surface was achieved (3.02 mmol $g^{-1}$). Oxidized multiwalled carbon nanotubes (45 mg) were loaded into a 35 mm × 4 mm (i.d.) PTFE-microcolumn plugged with a small portion of glass wool at both ends to avoid sorbent losses during the SPE. Prior to use, the column was cleaned and conditioned by passing through 2 mL of a 1.0 M solution of nitric acid followed by 4 mL of pure water.

### 2.4. Urine samples

Different fresh urine samples from healthy people with no history of exposure to lead were collected in acid-washed polypropylene bottles. Samples were prepared as follows. The appropriate amount of urine was treated with a 0.1 M solution of $HNO_3$ to pH 4.0 and it was diluted to 40% (v/v) before solid phase extraction and ETAAS-measurement. When the analysis was not immediately carried out the urine samples were stored at 4 °C (the storage period was kept as short as possible).

### 2.5. SPE–ETAAS analytical procedure

A 4 mL aliquot of urine sample, treated as indicated in Section 2.4, was passed through the microcolumn with a peristaltic pump at a flow rate of 1.1 mL $min^{-1}$ to achieve retention of the Pb ions by the MWCNTs. In the second step, 1.5 mL of a 0.1 M solution of $HNO_3$ was passed through the column at a flow rate of 0.6 mL $min^{-1}$ to eliminate the urine matrix. The retained Pb ions were subsequently eluted by employing 1.5 mL of a more concentrated 0.7 M $HNO_3$ solution (at a flow rate of 0.4 mL $min^{-1}$). 20 μL of this eluted solution sample was mixed with 2 μL of an aqueous matrix modifier solution containing 0.005% (w/v) $NH_4H_2PO_4$ and the resulting sample was subjected to ETAAS under the optimized conditions indicated in Table 1. All measurements were made in integrated absorbance mode. Eight microcolumns were used simultaneously for the SPE procedure.

## 3. Results and discussion

### 3.1. Optimization of the SPE

Different variables that influence the SPE retention of lead ions by MWCNTs packed in the microcolumn were studied. Since oxidized-carbon nanotubes lead to the formation of active hydroxyl, carbonyl and carboxyl groups on the surface of the MWCNT, it is evident that the pH of the solution passed through the column will affect the sorbent's structure as well as the degree of ionization and speciation of the adsorbates. In the present case, the pH range investigated was

**Table 1**
Furnace heating programs for ETAAS determination of lead.

| Step | Temperature (°C) | Ramp (s) | Hold (s) |
|---|---|---|---|
| Dry | 90 | 30 | 25 |
| Ash | 350 | 15 | 5 |
| Atomization[a] | 1550 | 1 | 3 |
| Clean | 2400 | 1 | 2 |
| Cold | 40 | 40 | 0 |

[a] Stop Ar flow.