An automated solid phase extraction coupled with electrothermal atomic absorption spectrometric determination of Pb(II) in high salt content samples

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ABSTRACT

A novel Pb(II) analysis in dialysis concentrates and seawater samples has been developed with on-line separation and preconcentration system coupled with electrothermal atomic absorption spectrometer (FI-ETAAS). Lewatit Monoplus TP207 imminodiacetat chelating resin was used for separation and pre-concentration of Pb(II) ions at pH 4.0. The influence of the analytical parameters such as type of eluent, flow rate of eluent and sample, eluent volume and matrix ions were investigated. W–Rh coated furnace was used as the atomization site. A preconcentration factor of 14 and a detection limit (3s/b) of $12\,ng\,L^{-1}$, along with the sampling frequency of $21\,h^{-1}$ were achieved with a $170\,s$ sample loading time and with $2.8\,mL$ sample consumption. The relative standard deviation (RSD) was 1.6% for $1\,\mu g\,L^{-1}$ Pb(II) level. The developed method was used for Pb(II) analysis in dialysis concentrates and seawater samples. The certified reference material (CRM403) experimental results are in good agreement with the certified value.

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1. Introduction

Lead is one of the natural components of the environment which include soil, water, air, vegetation and animal life. Lead is known to be a poison if absorbed into the bloodstream, especially in the case of inorganic lead, and is distributed to soft tissue, bones and teeth (95% in bones and teeth). Organic forms of lead are fat soluble and therefore have a particular tendency to concentrate in the brain [1]. A regular absorption of small quantities of lead may cause serious injuries to health such as encephalopathy, kidney damage and damage to the body in several other ways [2].

Many detection techniques such as spectrophotometry [3–5], flame atomic absorption spectrometry (FAAS) [6–9], electrothermal atomic absorption spectrometry (ETAAS) [10–12], inductively coupled plasma optical emission spectrometry (ICP-OES) [13], inductively coupled plasma mass spectrometry (ICP-MS) [14,15] and electroanalytical methods [16–18] have been used for detection of lead in various environmental samples.

ETAAS is the most commonly applied detection for low level of lead. However in high salt content matrices, especially alkaline chlorides, a high background signal, and depressed analyte signals due to loss on ashing steps as volatile lead chlorides, can

be seen. Formation of volatile lead chloride at low temperatures and deposition of chlorides at cooler ends of graphite tubes take place. As the temperature rises, revolatilisation and atomisation of deposited compounds result in formation of lead halides, reducing atomic signal as a result of vapour phase interferences. In addition, molecular absorption and scattering take place [19]. Therefore, the separation procedures should be applied in the analysis of high salt content samples which include low levels of analyte ions.

Several processes are currently in place for separation and preconcentration of Pb(II) including solvent extraction [20], new synthesis polymer beads [21], coprecipitation [22], single drop microextraction (SDME) [23,24], and dispersive liquid–liquid microextraction (DLLME) [25,26].

Lewatit MonoPlus TP207 is a high-capacity, weakly acidic, macroporous cation exchange resin with iminodiacetate functional groups. Also, it is used for the selective extraction of heavy metal cations from aqueous solutions. It has a total ion exchange capacity of $2.0\,meq/mL$, a particle size of $0.61 \pm 0.05\,mm$, and thermal stability of up to $313\,K$ [27]. The resin is a widely used chelating resin for separation and preconcentration of trace metal ions [27–32].

The aim of this paper was to develop a new labmade on-line separation/preconcentration and electrothermal atomic absorption spectrometric method for the determination of Pb(II) in high salt content samples such as dialysis concentrates. The system and the resin were firstly used for FI-ETAAS determination of Pb(II) in these samples.

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2. Experimental

2.1. Instrument

A Perkin-Elmer Model AA800 atomic absorption spectrometer (Norwalk, CT, USA) with a transversely heated graphite tube atomizer (THGA) and Zeeman-effect background correction, equipped with a Perkin-Elmer Model AS-800 furnace autosampler was used throughout the study. A lead hollow cathode lamp was used as the radiation source at the 283.3 nm wavelength with 12 mA lamp current and 0.7 nm slit width. Pyrolytic graphite-coated electrographite tube with an integrated L'vov platform coated with W–Rh described elsewhere was used [33]. The spectrometer was operated with integrated absorbance (peak area) values computed by the software of the instrument. The autosampler was used for online sampling from eluate solution. The stop and go intervals of the two peristaltic pumps and the actuation of the pinch valves were controlled automatically by using the six channel timer made in our instrumentation laboratory. Two peristaltic pumps (Ismatec Reglo, Germany) were used to propel all solutions and two pinch valves (Cole Parmer, USA) were used to select appropriate solutions for FI steps. A minicolumn filled with Lewatit MonoPlus TP207 iminodiacetic acid chelating resin was placed onto a sampling vessel. PVC pump tubes (0.8 mm i.d.) were used to pump sample, reagent, eluent and air. All the other tubings used were Teflon (0.5 mm i.d.) and "Y" and "T" joint connections used were HDPE material. All pH measurements were made with a Consort C533 model pH meter (Turnhout, Belgium) and a combination glass electrode.

2.2. Reagents

Ultrapure water was used to prepare all solutions. The hydrochloric acid was Suprapure (Merck, Darmstadt, Germany). Lewatit MonoPlus TP207 resin (Fluka, Milwaukee, USA) was used after 2 h drying in an oven at 110 °C. All other reagents were of analytical reagent grade. The laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with ultrapure water. Pb(II) stock solution ($100 \,\mu g \, L^{-1}$) was prepared by diluting of $1000 \, mg \, L^{-1}$ atomic standard lead solution (Merck, Darmstadt, Germany) with a $1 \, mol \, L^{-1}$ hydrochloric acid solution. Acetate buffer solution (pH 4.0) was prepared by dissolving 136 g of $CH_3COONa \cdot 3H_2O$ and 4.7 mL of concentrated CH_3COOH (Merck, Darmstadt, Germany) in 1000 mL of deionized water. Hydrochloric acid ($2.0 \, mol \, L^{-1}$) was prepared by direct dilution with deionized water from the concentrated suprapur solution. 8.0 g of NaOH (Merck, Darmstadt, Germany) was dissolved and filled to 100 mL with ultrapure water in a volumetric flask.

2.3. Column preparation

The resin was cooled in a desiccator and weighed 20 mg in a glass beaker. It was made slurry with water and filled in a glass minicolumn (20 mm × 2 mm) with a micropipette tip. The resin was covered with a glasswool to avoid disturbance of the resin path.

2.4. Sample preparation

Diasol K2 Ac2 acidic hemodialysis concentrates (DC_1–DC_5), Lot No.:5–9, (NaCl:214.77 g, KCl:5.22 g, $CaCl_2 \cdot 2H_2O$:7.72 g, $MgCl_2 \cdot 6H_2O$:3.55 g, CH_3COOH:4.20 g in 1000 mL solution) were purchased from a local drug producing company. 10 mL of concentrate was pipetted in a glass beaker and pH was adjusted to 4.0 with $2 \, mol \, L^{-1}$ NaOH solution and filled to 100 mL in a volumetric flask.

Seawater samples were collected from the coastal areas of İzmir (S_1), İstanbul (S_2) and Antalya (S_3) from Turkey. Samples were
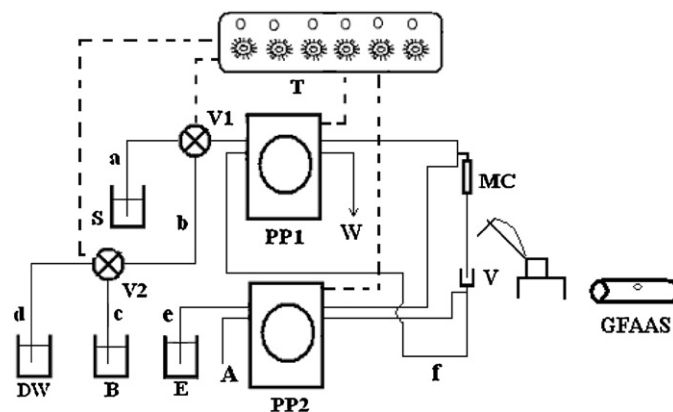

Fig. 1. FI manifold and its operation steps. (PP1 and PP2: sample and eluent pumps respectively; V1 and V2: pinch valves; MC: minicolumn; T: timer, W: waste; V: vial in autosampler; S: sample; A: air; E: eluent; B: buffer solution; DW: deionized water; a, b, c, d, e and f: solution ways.)

acidified with 50 mL of concentrated HNO_3 for 5 L of sample and stored in +4 °C. Before use, 50 mL of sample was pipetted into a glass beaker and the pH was adjusted to approximately 4.0 with $2 \, mol \, L^{-1}$ NaOH solution and 10 mL buffer solution. The solution was then increased to volume of 100 mL in a volumetric flask.

CRM403 seawater certified reference material (CRM) was prepared as real seawater samples.

2.5. On-line preconcentration system

The diagram of the on-line preconcentration system is shown in Fig. 1. The performance of the FI-ETAAS preconcentration method was tested with model solutions before application to the real samples.

In step 1, PP1 and V1 were active while PP2 and V2 were inactive, and the sample and/or standard solutions adjusted to a pH of 4.0 were continuously passed through the minicolumn (MC) for 2.5 min at a flow rate of $1 \, mL \, min^{-1}$. The Pb(II) ions were retained on the minicolumn while the effluent was disposed of as waste. The effluent solution was removed from the elution vessel by the discharge tubing on the same pump.

In step 2, the minicolumn was washed with water in order to remove matrix ions from the resin. At this period, PP1 and V2 were active while PP2 and V1 were inactive.

In step 3 (in the elution step) the eluent, $200 \,\mu L$ of $2 \, mol \, L^{-1}$ HCl, was pumped to the vessel by the PP2 at a flow rate of $0.6 \, mL \, min^{-1}$. During elution, PP1 was inactive. In the same time, the air bubbles provided by air tubing on the pump were used for eluate homogenization.

In step 4, there was no action in the flow system. In this step, $20 \,\mu L$ eluate mixed with air bubbles was pipetted and after injected to the W–Rh coated platform of the furnace. The furnace program of the ETAAS is shown in Table 1.

In step 5, the minicolumn was washed with water (PP1 and V2 were active, PP2 and V1 were inactive) for cleaning the resin to avoid a large consumption of buffer solution.

In step 6, the buffer solution was pumped to the column to condition it before a new preconcentration cycle. During this period, PP1 was active while PP2, V1 and V2 were inactive. Subsequently, the system began the cycle again automatically.

3. Results and discussion

The optimised chemical and hydrodynamic conditions in the flow system were determined by using a solution involving $1 \,\mu g \, L^{-1}$