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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 preconcentration 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 μg 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.

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 ± 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 on-line 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 μg 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 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.

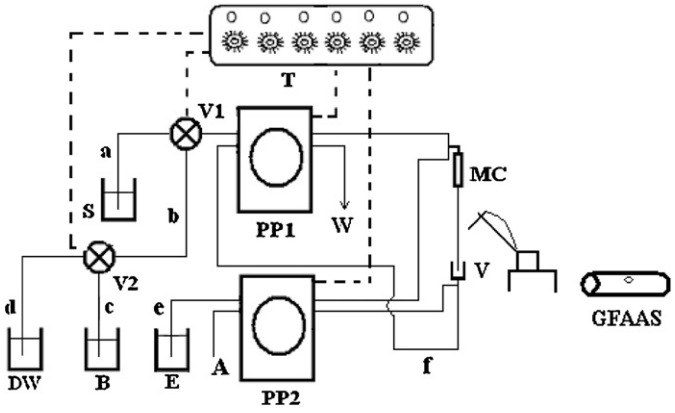

Fig. 1. FI manifold and its operation steps. (PP1 and PP2: sample and eluent pumps respectively; *V*1 and *V*2: pinch valves; MC: minicolumn; *T*: timer, W: waste; V: vial in autosampler; *S*: sample; A: air; E: eluent; B: buffer solution; DW: deionized water; a, b, c, d, e and f: solution ways.)

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 *V*1 were active while PP2 and *V*2 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 *V*2 were active while PP2 and *V*1 were inactive.

In step 3 (in the elution step) the eluent, 200 μL 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 μL 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 *V*2 were active, PP2 and *V*1 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, *V*1 and *V*2 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 μg L^{-1}

Table 1
Graphite furnace temperature/time programme for the determination of Pb (II).

Step	Temperature (°C)	Ramp time (s)	Hold Time (s)	Ar flow rate (mL min^{-1})
Drying	110	1	30	250
Drying	130	15	30	250
Ashing	900	15	15	250
Atomization	1400	0	5	0
Cleaning	2450	1	3	250

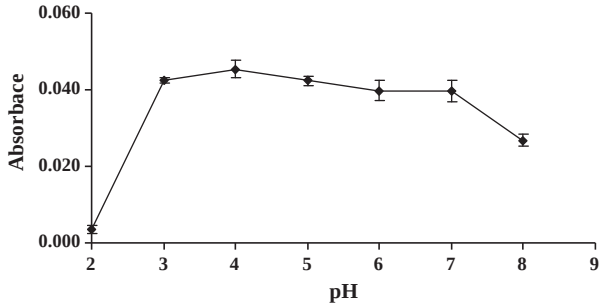

Fig. 2. The effect of the pH of sample on the lead signals. (Lead concentration: 1 μg L^{-1}; preconcentration time: 170 s; sample flow rate: 1.0 mL min^{-1}; eluent flow rate: 0.6 mL min^{-1}; eluent volume: 300 μL.)

Pb(II) and the preconcentration procedure was applied to the aqueous sample solutions.

3.1. Effect of pH

The pH value of the medium affects to complexation of the analyte and chelating agent. The formation constants of complexes depend on the pH of the medium. Therefore pH is very important parameter for retention of the analyte ions on the surface of solid phase with the complexation mechanism. The effect of sample pH on the Pb(II) signals was investigated within the pH range of 2.0–8.0. In this study, Pb(II) ions were chelated by iminodiacetate groups in the pH range of 3.0–7.0. As can be seen in Fig. 2, pH 4.0 was selected for all further work.

3.2. Effects of eluent type and concentration

The elution of Pb(II) from the minicolumn was studied by using hydrochloric acid and nitric acid solutions at different concentrations (0.1–6.0 mol L^{-1}). For this experiment, the retained Pb(II) was eluted with 350 μL of different eluent solutions and blank corrected signals showed that the most suitable eluent was 2.0 mol L^{-1} hydrochloric acid. These results indicate that the Pb(II) elution with hydrochloric acid is more effective than nitric acid because of the chloro complexes formation of the Pb(II) ions ($PbCl^+$, $PbCl_3^-$, and $PbCl_4^{2-}$) during the elution. The results are shown in Fig. 3.

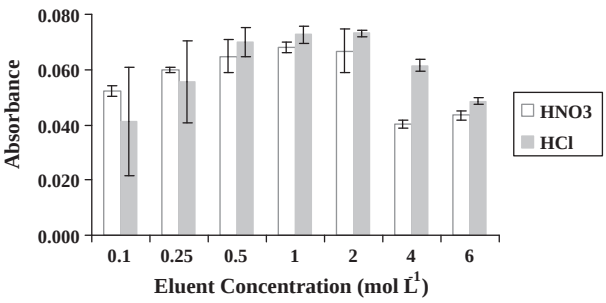

Fig. 3. Effects of eluent type and concentrations on the elution efficiency. (Lead concentration: 1 μg L^{-1}; preconcentration time: 170 s; sample flow rate: 1.0 mL min^{-1}; eluent flow rate: 0.6 mL min^{-1}; eluent volume: 300 μL.)

3.3. Effects of eluent volume

The eluent volume is important for quantitative recovery of the analyte. For that reason, the effect of the eluent volume was studied in the range of 140–570 μL. When the elution time taken was short, the elution volume was small. In this case, the analytical signals were also low due to insufficient elution of the retained Pb(II) ions. The optimum eluent volume for quantitative elution of Pb(II) was 200 μL.

3.4. Effects of flow rate of sample and eluent solutions

The sample flow rate is an important parameter in on-line systems because it affects the retention of the cation on the minicolumn. At high flow rates of sample, metal ions could probably not equilibrate properly with the resin due to the increase in the velocity of the ions, which reduces the contact time between the two phases. In contrast, low flow rates decrease throughput the sample, resulting in long analysis times. For this reason, the effect of sample flow rate on the sorption of Pb(II) was investigated. The results are shown in Fig. 4. The signals obtained from the Pb(II) ions increased up to 1 mL min^{-1} because of the suitable contact time between two phases. On the other hand, the signals decreased in case of the higher flow rates. Because, the flow rates were too fast for quantitative retention of Pb(II).

Consequently, the optimum flow rate of sample was chosen to be 1 mL min^{-1} in subsequent experiments as a compromise between efficiency and stability.

The influence of the 2.0 mol L^{-1} hydrochloric acid solution flow rate in the step of Pb(II) desorption from the minicolumn was also investigated. According to Fig. 5., the best results were obtained in flow rate of 0.6 mL min^{-1}. All of the signals were multiplied with dilution factor. At flow rates more than 0.6 mL min^{-1} the analytical signals decreased. These results indicate that the Pb(II) elution is minor at high flow rates, probably, because the eluent solution passes through the column too quickly for the contact time between the phases to be sufficient for significant elution.

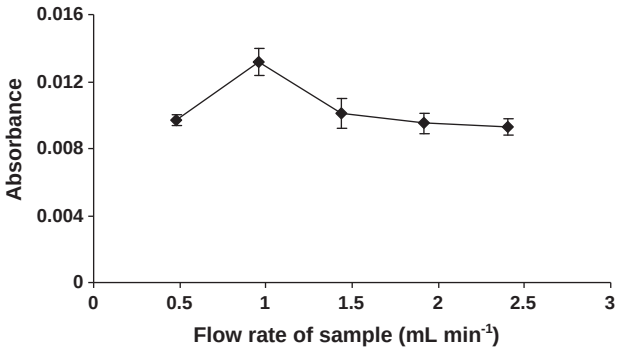

Fig. 4. Effects of flow rate of sample solution on retention efficiency. (Lead concentration: 1 μg L^{-1}; preconcentration time: 170 s; eluent flow rate: 0.6 mL min^{-1}; eluent volume: 200 μL.)

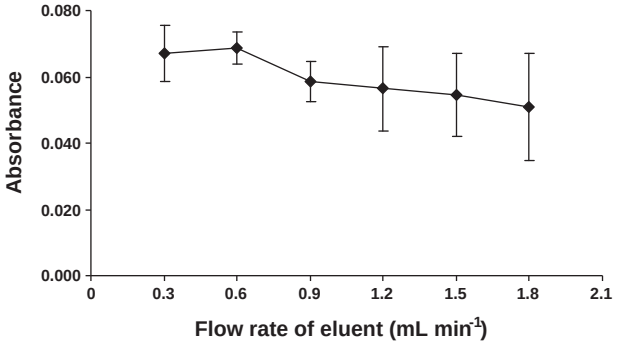

Fig. 5. Effects of flow rate of eluent solution on elution efficiency. (Lead concentration: 1 μg L^{-1}; preconcentration time: 170 s; sample flow rate: 1.0 mL min^{-1}; eluent volume: 200 μL.)

Table 2
The effect of interferences on the retention of Pb(II) (N = 3).

Interferent	Added as	Concentration (mg L^{-1})	% R[a]
Na^+	$NaNO_3$	23,000	96 ± 1
K^+	KNO_3	10,000	98 ± 1
Ca^{2+}	$Ca(NO_3)_2{\cdot}4H_2O$	5,000	101 ± 2
Mg^{2+}	$Mg(NO_3)_2{\cdot}6H_2O$	2,500	96 ± 1
SO_4^{2-}	Na_2SO_4	8,000	98 ± 1
Cl^-	NaCl	35,500	102 ± 2

[a] $\bar{x} \pm s$.

3.5. Effects of amount of resin

In solid phase extraction experiments, the resin quantity is a very important factor for quantitative recovery of analyte ions. In low quantities, analyte ions can pass through the column without retention. In contrast, the eluent volume can be insufficient for quantitative elution of the analyte ions. Therefore, the effect of the amount of resin on the sorption of Pb(II) was investigated by varying amounts (10–40 mg). As can be seen in Fig. 6., the optimum amount of resin was chosen as 30 mg.

3.6. Effect of foreign ions

The effect of foreign ions on the determination of Pb(II) was investigated using the optimized on-line preconcentration system. Foreign ions were added individually to model solutions containing 1 μg L^{-1} Pb(II) and then the proposed procedure was applied. The effect of each species was considered as interference when the analytical signal in the presence of the species resulted in an absorbance deviation of more than ±5%. The results are shown in Table 2. The results indicate that various substances commonly present in seawater and dialysis concentrate samples do not interfere in the analysis of Pb(II) under experimental conditions.

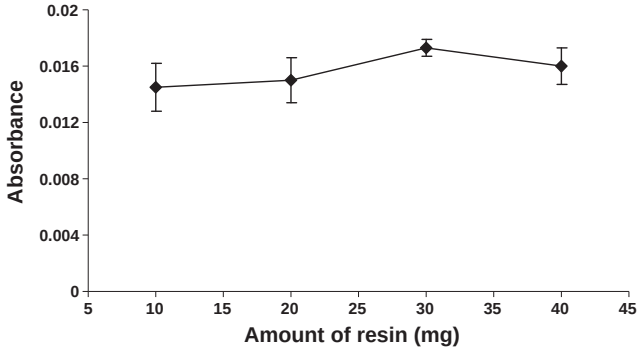

Fig. 6. Effects of amount of resin. (Lead concentration: 1 μg L^{-1}; preconcentration time: 170 s; sample flow rate: 1.0 mL min^{-1}; eluent flow rate: 0.6 mL min^{-1}; eluent volume: 200 μL.)

Table 3
Results of the determination of Pb(II) in CRM403 certified seawater sample (N = 3).

CRM	Certified value (μg L^{-1})	Found[a] (μg L^{-1})	% Recovery
CRM-403 seawater	0.024 ± 0.005	0.025 ± 0.003	104 ± 12

[a] $\bar{x} \pm \frac{ts}{\sqrt{N}}$, 95% confidence level.

3.7. Analytical figures of merit

The characteristic data for the performance of the on-line preconcentration system under the optimum conditions were studied. Linear regression equations were obtained for calibration curve in the range of 0.05–5.0 μg L^{-1}, i.e., $A = 0.1005 \times C_{Pb(II)} - 0.0006$, where A is the absorbance and $C_{Pb(II)}$ is the Pb(II) concentration in the standard solution. Enrichment factor was found to be 14. The detection limit based on 3σ of the blank solution was 12 ng L^{-1} (N = 21) and limit of quantification was calculated as 40 ng L^{-1}. A precision of 1.6% for the concentration of 1.0 μg L^{-1} Pb(II) was calculated.

3.8. Accuracy of the method

The accuracy of the developed method was tested by measuring the Pb(II) content in the CRM403 seawater certified reference material (CRM). The Pb(II) contents established with the present procedure agreed very well with the certified values (Table 3). The results indicate that the developed procedure can be applied to the determination of Pb(II) in the certified seawater samples being free from interference.

3.9. Application of the proposed procedure

The method was extended for the on-line determination of Pb(II) in high salt content samples as seawater and dialysis concentrates. Preparation of the samples to be analysed was performed as described above in Section 2.4. The results are shown in Table 4. The proposed method was applied to the analysis of the samples, with satisfactory results for Pb(II). The concentration of Pb(II) could not be determined due to its very low concentration in CRM. To overcome this fault, the sample was passed for 28 min (10 fold) through the minicolumn. The recoveries for the additions of 0.5

Table 4
Results for the determination of Pb(II) in seawater (S) and dialysis concentrate (DC) samples (N = 3).

Sample	Added (μg L^{-1})	Found[a] (μg L^{-1})	% Recovery
DC_1	–	17.0 ± 0.3	–
	10.0	26.5 ± 0.6	97 ± 2
DC_2	–	18.2 ± 0.2	–
	10.0	28.3 ± 0.4	100 ± 1
DC_3	–	36.4 ± 0.1	–
	10.0	45.9 ± 0.6	99 ± 2
DC_4	–	26.2 ± 0.2	–
	10.0	36.6 ± 0.7	101 ± 2
DC_5	–	21.0 ± 0.3	–
	10.0	29.8 ± 0.4	96 ± 1
S_1	–	0.12 ± 0.01	–
	0.5	0.60 ± 0.02	97 ± 4
S_2	–	0.26 ± 0.01	–
	0.5	0.78 ± 0.02	103 ± 3
S_3	–	0.10 ± 0.01	–
	0.5	0.61 ± 0.01	102 ± 2

[a] $\bar{x} \pm s$.

and 10 $\mu g\,L^{-1}$ Pb(II) varied from 96% to 103% (see Table 4). These results prove the validity of the proposed method. There was a good agreement between the added and the recovered amounts of the analyte.

4. Conclusions

The results in this work demonstrate the feasibility of on-line coupling of a FI sorption preconcentration system with a solid phase extractor to ETAAS for fully automatic determination of $\mu g\,L^{-1}$ levels of Pb(II) in high salt content samples. With the use of the developed FI system, the consumption of the eluent was greatly reduced. The system permitted the use of high sample loading rates to achieve high enhancement factors and low costs as it was lab-made. The new method had low detection ($ng\,L^{-1}$) limit, easy to form in many laboratories and wide sample variation because of interference free.

Although direct analysis of samples in ETAAS is easy, high salt content samples cannot be analysed directly because of many interference effects. This system minimizes the analysis time and manpower needed in laboratories compared to offline systems.

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