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LEAD PRE-CONCENTRATION USING SOLID PHASE EXTRACTION

Alina CULEȚU[1], Alina Catrinel ION[2], Ion ION[3], Constantin LUCA[4]

Plumbul este recunoscut la nivel mondial ca fiind un metal nociv, din cauza efectelor sale negative. Astfel, determinarea acestui element este de obicei necesară în probele de mediu şi alimente. Totuşi, aceste analize sunt greu de realizat, deoarece astfel de probe conțin plumb la nivel de urme, care poate fi sub limita de detecție a metodelor analitice tradiționale. Extracția în fază solidă este recomandată pentru pre-concentrarea urmelor de plumb din probe.

Scopul acestei lucrări este de a pre-concentra cantitativ plumbul pe Chelex 100, optimizând diverşi parametrii precum pH, concentrația şi volumul eluentului, cantitatea de răşină şi volumul probei. Plumbul a fost determinat potențiometric folosind electrozi ion-selectivi construiți în laboratorul nostru.

Lead is recognized worldwide as a poisonous metal, due to its negative effects. Thus, the determination of this element is often required in environmental and food samples. However, these analyses are difficult because such samples contain lead at trace level, which may be lower than the detection limit of conventional analytical techniques. Solid phase extraction is recommended for the pre-concentration of traces of lead from sample matrices.

The aim of this study is to quantitatively pre-concentrate the lead on Chelex 100, optimizing various parameters such as pH, concentration and volume of the eluent, amount of resin and volume of sample solution. Lead was potentiometrically determined using ion-selective electrodes designed in our laboratory.

Keywords: solid phase extraction, lead, ion-selective electrode, Chelex resin

1. Introduction

Due to negative effects of lead ions for human health [1], lead pollution in the food and the environment represents an important problem [2].

The determination of trace lead metal ions presents some difficulties such as: low concentration of lead ions, which may be lower than the detection limit of

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[1] PhD student, Department of Analytical Chemistry and Instrumental Analysis, University POLITEHNICA of Bucharest, Romania, e-mail: alinaculetu@yahoo.com

[2] Prof., Department of Analytical Chemistry and Instrumental Analysis, University POLITEHNICA of Bucharest, Romania

[3] Prof., Department of Analytical Chemistry and Instrumental Analysis, University POLITEHNICA of Bucharest, Romania

[4] Prof., Department of Analytical Chemistry and Instrumental Analysis, University POLITEHNICA of Bucharest, Romania

many analytical techniques and the possible interferents from the environment and food are the most important.

Various methods are recommended for the pre-concentration of trace lead from sample matrices, such as: solvent extraction [3, 4], electroanalytical techniques [5], membrane filtration [6,7] and solid phase extraction (SPE) [8-13]. Of all the techniques mentioned above, SPE presents some advantages: sensitivity, large pre-concentration factors, simplicity of phase separation, low consumption of reagents.

Sorbents used in the pre-concentration for lead determination include: Chelex 100 [14], Amberlite XAD resins [15, 16], activated carbon [17], natural adsorbents [18], silica gel [19], and cellulose [20].

This paper describes a pre-concentration procedure based on solid phase extraction of lead using Chelex 100 resin. In order to determine the optimum conditions for quantitative recovery of lead, various analytical parameters such as: pH, concentration and volume of eluent, amount of resin and volume of sample solution were investigated.

2. Experimental

2.1. Apparatus

Potentiometric measurements were conducted using a potentiometric interface ELITE 8908 with 8 channels (NICCO, UK) and the cell assembly was:

Ag | AgCl | internal solution || PVC membrane || sample | Ag | AgCl | KCl.

Pb(II)-selective sensor was fabricated by our group based on previous studies [21] from PVC matrix membranes containing 3,7,11 - tris (2-pyridylmethyl)- 3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene as ionophore. The sensor can be used in a concentration range 10^{-6} - 10^{-1} M and pH range from 5 – 8 [22].

pH measurements in the aqueous phase were made by means of a digital PHM240 pH/ion meter (MeterLab Radiometer Analytical).

2.2. Reagents and materials

All chemicals used were of analytical grade and purchased from Merck (Darmstadt, Germany). The working solutions were prepared with doubly distilled water.

Chelex 100 (100-200 mesh) (Bio-Rad Laboratories, Richmond, CA, USA) is a styrene divinylbenzene copolymer containing paired iminodiacetate ions which act as chelating groups in binding polyvalent metal ions. Chelex resin is classed as a weakly acidic cation exchange resin by virtue of its carboxylic acid groups, but it differs from ordinary exchangers because of its high selectivity for metal ions and its much higher bond strength.

Chelex resin operates in basic, neutral and weakly acidic solution of pH 4 or higher. At very low pH, the resin acts as an anion exchanger. Fig. 1 shows the ionic forms of the Chelex resin as a function of pH.

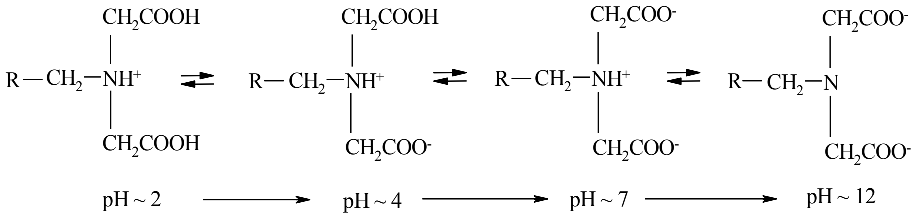

Fig. 1. Change in structure of Chelex resin with increasing pH

Prior to use Chelex, resin was successively washed with 5M nitric acid and rinsed with doubly distilled water, in order to eliminate trace metal ions and other inorganic and organic contaminants in the resin.

2.3. Pre-concentration procedure

For the batch method, an aliquot of dry resin (0.5000 g) and 50 mL of aqueous phase were transferred in a 150 mL flask and shaked for 1 h. For the column method, a column was poured with the Chelex resin and the sample was passed through to achieve the separation. The metal concentrations in the solution were determined by potentiometric measurements using a lead-selective electrode. The pH of the solutions was adjusted with 0.1 M HNO_3 and 0.1 M NaOH.

The capacity of the resins determined according to [23] was found to be of 2.0 mmol/g of dry resin Chelex 100 in H^+ form.

3. Results and discussion

The effect of contact time on the sorption

The necessary contact time between the resin and lead ions for an optimal sorption was varied from 5 to 60 min, and the results are shown in Fig. 2. For a sorption degree of 99%, a contact time of 60 minutes was selected as optimum contact time and applied during all studies. The metal uptake versus time curves, suggests the possible monolayer coverage of metal ions on the surface of the sorbent.

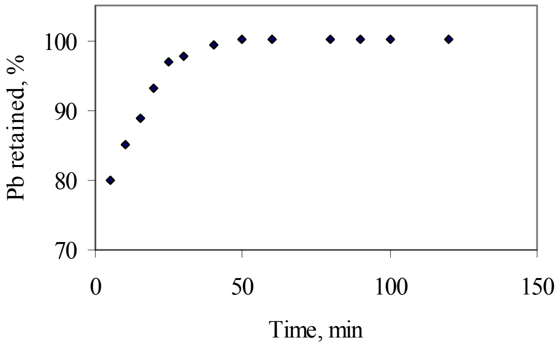

Fig.2. Effect of contact time on sorption (batch method).
Experimental conditions: 12 ppm Pb(II); 0.5 g Chelex 100; 50 mL volume of solution.

The influence of pH on sorption

For solid phase extraction of the heavy metal ions on different type of chelating resins, the pH of the aqueous solution is one of the main factors for quantitative recoveries of the analytes [24]. Due to this important point, the influence of pH was investigated in a pH range of 2–8. The correlation between the degree of the adsorbed lead on the resin and pH is presented in Fig. 3. The results of this study showed that lead ions were completely adsorbed on the sorbent over the pH range of 3.5 – 7.

Therefore, pH 6.0 was chosen as the optimum pH for further studies.

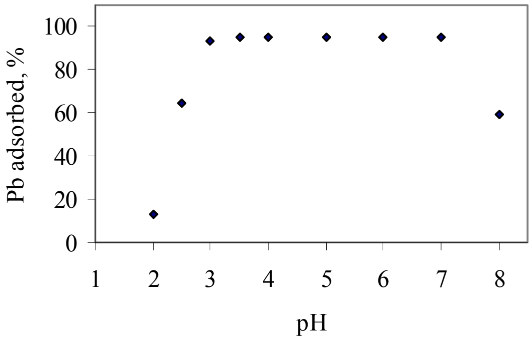

Fig.3. The effect of the pH of sample on the sorption of lead (bach method).
Experimental conditions: 12 ppm Pb(II); 0.5 g Chelex 100; 50 mL volume of solution.

Effect of the eluent concentration and its volume

Various concentrations of nitric acid were examined to obtain quantitative recovery values for lead from Chelex 100 (Fig. 4). The recoveries were not quantitative when the concentration of nitric acid less than 1 M was used as an eluent. 1.5 M HNO_3 was used for quantitative recovery of lead from Chelex 100 in further studies.

The volume of the eluent (1.5 M HNO_3) that can completely strip the retained lead from the solid phase is an important parameter for obtaining the maximum pre-concentration factor. Thus, some experiments were carried out in order to choose a proper eluent volume for retaining the lead ions on Chelex 100 (Fig. 5). The recovery values for lead ions from the Chelex column were greater than 95% in the eluent volume range of 15 – 50 mL. In an eluent volume lower than 15 mL, the recovery of lead ion was not quantitative, because of insufficient eluent volume.

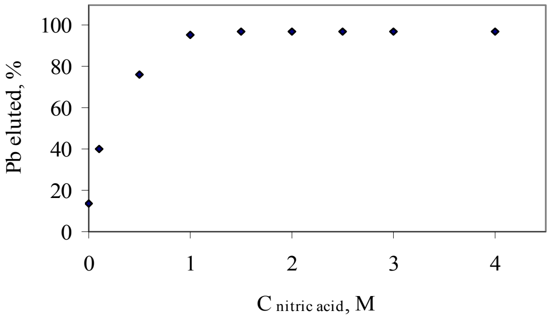

Fig. 4. Influence of the concentration of nitric acid over the desorption (column method). Experimental conditions: 12 ppm Pb(II); 0.5 g Chelex 100; 50 mL volume of solution

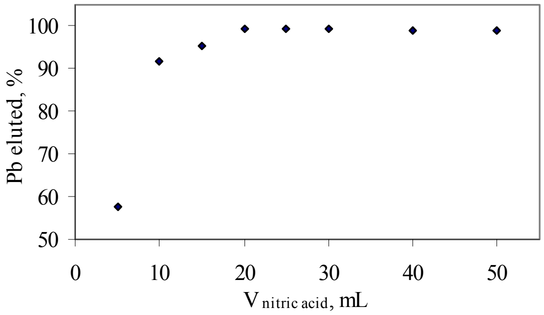

Fig. 5. Influence of the volume of nitric acid over the elution of lead ions (column method). Experimental conditions: 12 ppm Pb(II); 0.5 g Chelex 100; 1.5 M HNO_3; 50 mL volume of solution

Effect of the Chelex resin amount

The amount of solid phase extraction material is another important factor on the sorption studies for the quantitative recoveries of metal chelates [25]. The effect of the amount of Chelex 100 on the sorption of lead ions was examined in the range of (0.1 – 1) g (Fig. 6). The results demonstrated that, quantitative recoveries (>95%) of lead were observed when the resin was used above 0.4 mg.

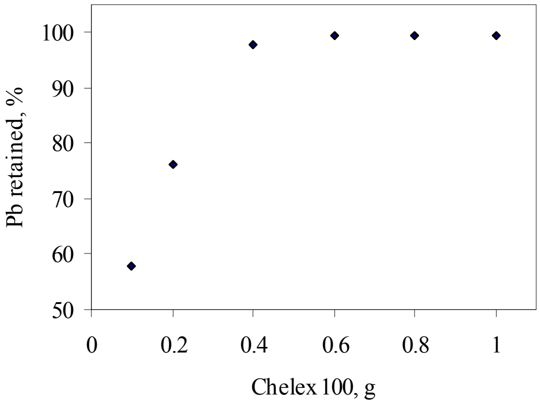

Fig. 6. Optimization of the amount of resin used (batch method).
Experimental condition: 12 ppm Pb(II); 50 mL volume of solution

Effect of sample volume on column experiment

The effect of sample volume on the adsorption of lead ions on 0.5 g Chelex was investigated by passing sample volumes of 10-500 mL containing 12 ppm Pb(II) through the column.

The results are shown in Fig. 7. At volumes higher than 150 mL, the recovery for lead was not quantitative. The pre-concentration factor for simultaneous pre-concentration and extraction is calculated by the ratio of the highest sample volume for lead (500mL) and the lowest final eluent volume (10mL). In present study, the possible pre-concentration factor was 50.

The results show that Pb(II) up to the volume of 150 mL were quantitatively recovered.

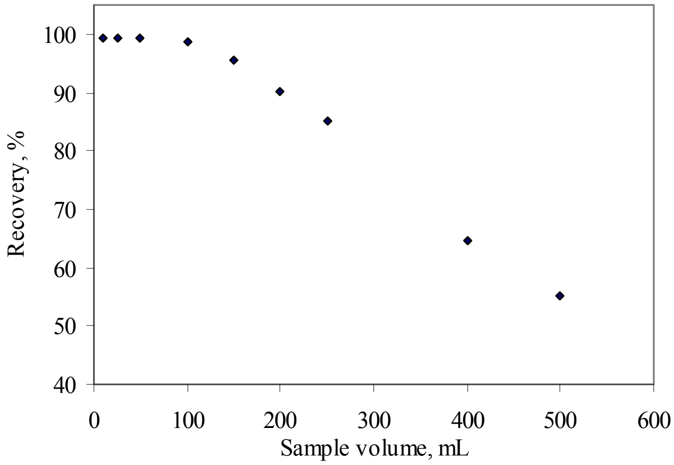

Fig. 7. The influences of the sample volume on the retention of Pb(II) from Chelex 100 (column method).

Experimental conditions: 12 ppm Pb(II); 0.5 g Chelex 100; 50 mL volume of solution

4. Conclusions

Considering the poisonous nature of lead and the low concentration of this element in samples, in our study solid phase extraction was used as pre-concentration technique for aqueous samples. The experiments were run both in batch and column techniques, optimal results being obtained in both.

Quantitative recoveries of lead on Chelex 100 were optimized by varying different parameters such as pH, concentration and volume of the eluent, the amount of resin and volume of sample solution. This study will be continued in order to potentiometrically determine lead from environmental aqueous samples at trace level in the presence of several interferents, using the new lead electrode obtained in our laboratory.

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