

## OPTIMIZATION OF PRECONCENTRATION OF CADMIUM AND LEAD FROM SAMPLES WITH PHOSPHATE MATRICES USING CHELEX 100

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In this study, iminodiacetate type of chelating resins (Chelex 100) were used for collecting metal ions, which enhance the adsorption efficiency for metal species present in samples of phosphate nature such as NPK fertilizers. These preliminary results present a possibility of optimization for the preconcentration of Cd(II) and Pb(II) from phosphate matrices on Chelex 100.

### INTRODUCTION

The determination of trace- or ultra-trace amounts of elements becomes more and more important in fields such as environmental, biological and material sciences.<sup>1</sup> However, it is very difficult to determine trace- and ultra-trace elements directly even by the highly sensitive instruments now available because the detection sensitivity is sometimes insufficient and the effect of sample matrices in can not be neglected.

The preconcentration methods using chelating resins have increasingly replaced the traditional liquid-liquid extraction methods which generally use great amounts of organic solvents to obtain high enrichment factors and require laborious processes.<sup>2</sup>

Sorption on chelating resins is efficient for separation and concentration of metal ions prior to their determination. Iminodiacetate (IDA)-type chelating resins ( $-L^{2-}$ ) are commercially available and widely used. Recently, based on a Gibbs - Donnan model, the adsorption equilibrium of divalent metal ions ( $M^{2+}$ ) on IDA-type resins have been studied.<sup>3</sup> Based on this model, the adsorption equilibrium of divalent metallic ions ( $M^{2+}$ ) on chelating resins with iminodiacetic groups (IDA type) were studied.<sup>4-6</sup> A competitive method of protonation was adopted taking into account that the total concentration of functional groups is bigger than the concentration of metallic ions ( $C_{totL} > C_{totM}$ ). It was observed that the adsorption constants for  $[(HL)_2M^{II}]$  complexes are the same with the stability constants of IDA –  $Me^{2+}$  complexes in aqueous solution.<sup>7-9</sup>

During last years, behavior of heavy metals in soils was carefully studied.<sup>10</sup> Heavy metals in soils constitute an important source for their uptake by plants and subsequent input into the food chain. Environmental pollution, due to increasing chemical fertilization is one of the most effective factors of destruction of biosphere components. Among all, heavy metals in soils and subsequently in plants are considered potential hazardous contaminants of human health.<sup>11</sup>

For the determination of low level elements, pre-concentration and separation techniques are employed. Traces of cadmium and lead in different samples have been determined by neutron activation analysis,<sup>12</sup> inductively coupled plasma-atomic emission spectrometry (ICP-AES),<sup>13-15</sup> ion chromatography,<sup>16</sup> electrochemical methods,<sup>17, 18</sup> graphite furnace atomic absorption spectrometry (GFA-AAS)<sup>19-21</sup> and inductively coupled plasma-mass spectrometry (ICP-MS).<sup>22</sup>

The maximum admissible limits for heavy metals accumulation in soils are: 3 ppm for cadmium and 100 ppm for lead,<sup>23</sup> their concentration depending on phosphate source and on phosphor content in fertilizers. The content of cadmium and lead in fertilizers varies between 2-18 ppm in DAP (diammonium phosphate) and 180 ppm in TSP (triple super phosphate) for cadmium and 10-30 ppm in DAP and < 500 ppm in TSP for lead.<sup>24</sup>

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Cadmium has no influence over biochemical functions of organisms, but it has a toxic, cumulative effect by inhibiting the enzymatic systems (blocking the thiolic groups).<sup>25</sup> Lead is a non-essential element with toxic effect on the human health. At biochemical level, lead is capable to inhibit enzymes in the hem pathway and disturb the porphyrin metabolism.<sup>26</sup>

Our group has worked before in Cd(II) determination<sup>27</sup> from certain types of fertilizers using both potentiometry<sup>28,29</sup> and atomic absorption spectrometry with a different pre concentration technique.

In this study, iminodiacetate type of chelating resins (Chelex 100) were used for collecting metal ions, which enhance the adsorption efficiency for metal species present in samples of phosphate nature such as NPK fertilizers.

These preliminary results present a possibility of optimization of the preconcentration of heavy metals from phosphate matrices on Chelex 100.

## EXPERIMENTAL

### Apparatus

The measurements were carried out by atomic absorption spectrometry (AAS) on a Unicam Solaar 99 atomic absorption spectrometer with graphite furnace GF 90+ with furnace auto sampler SS 99. The determination of Cd(II) and Pb(II) were performed using calibration curves based on peak height measurements of calibration standards at 228.8 and 217.0 nm, respectively. A Methrom pH-meter was used for pH measurements equipped with a Methrom pH electrode and a Methrom Ag/AgCl in 3M KCl, as reference electrode.

### Reagents

All chemicals were of analytical reagent grade. Cd(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, KNO<sub>3</sub>, NaNO<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub> and other inorganic chemicals including HNO<sub>3</sub> and NaOH were purchased from Merck Co.

Chelating resin. Chelex 100 (100-200 mesh) (Bio-Rad Laboratories, Richmond, CA, USA) was selected. It was purified prior to use by successive washings with 5M nitric acid and rinsed with doubly deionized water.

Eluent. A 2M solution of nitric acid was prepared from concentrated nitric acid (65%) of Suprapur grade (Merck, Darmstadt, Germany) by dilution with doubly de-ionized water. No further purification of the eluent was performed.

Standard solutions. Cadmium, lead and calcium working standard solutions were prepared by appropriate dilution of stock standard solution containing 1.0000 gL<sup>-1</sup> Cd(II), 1.0000 gL<sup>-1</sup> Pb(II), 1.0000 gL<sup>-1</sup> Ca(II), respectively.

All laboratory ware was thoroughly cleaned with nitric acid (1:1), rinsed with doubly de-ionized water, further cleaned with hot aqueous 0.05% ammoniumtetramethylenedithiocarbamate (APDC) and rinsed again.

### Procedure

In the exchange experiments, an aliquot of dry resin (~ 0,5000 g) and 25 mL of aqueous phase were placed in a 125 mL glass - stoppered flask and shaken at 120 rpm for 48 h in a shaker (Heidolph). The shaker bath was controlled at several fixed temperatures (25 °C). After equilibrium, the concentration of metals in the aqueous phase were analyzed by AAS. The initial aqueous pH was adjusted by adding a small amount of 0.1 mol/L HNO<sub>3</sub> or 0.1 mol/L NaOH.

Each experiment was at least duplicated under identical conditions. The reproducibility of the measurements was within 3.5%.

The capacity of resins (mmol of active groups per g of dry resin) was found to be 2.0 mmol per g of dry resin Chelex 100 in H<sup>+</sup> form. It was determined as described elsewhere.<sup>3</sup>

NPK samples were prepared as in previous work.<sup>30</sup> 100 mL of extract were passed through the resin from the cartridge. After preconcentration, Cd(II) and Pb(II) were eluted in 5 mL 1.5M HNO<sub>3</sub> and determined by AAS.<sup>30</sup>

## RESULTS AND DISCUSSION

The effect of time on the sorption. Fig. 1 illustrates the sorption of Cd(II), Pb(II) and Ca(II) on Chelex 100 as time function.. The contact time between the resin and the metallic ions necessary for an optimal sorption was determined. For a sorption degree of 99%, a contact time of 55-60 minutes for Cd(II) and Pb(II) and 80 minutes for Ca(II) is necessary. The metal uptake versus time curves, suggest the possible monolayer coverage of metal ions on the surface of the sorbent.

The effect of pH. The variable that has the most significant effect on the affinity of a resin for a particular ion is pH. The chelating ion exchanger with iminodiacetic acid groups have showing complexation properties forming heterocyclic chelates with studied cations. The pH value of the solution is an important factor that controls the sorption of Cd(II) and Pb(II). The ratio of metal ion sorbed to total metal ion is reported vs. pH in range 1-10. A fixed amount of Chelex 100 was introduced in a fixed volume of

aqueous solution containing known amounts of Cd(II) and Pb(II) at fixed ionic compositions. The pH was changed by addition of small amount of concentrated acid or base and it was measured after the equilibrium was established (1 h at 25 °C). The concentration of metal ion in the aqueous phase was determined by AAS.

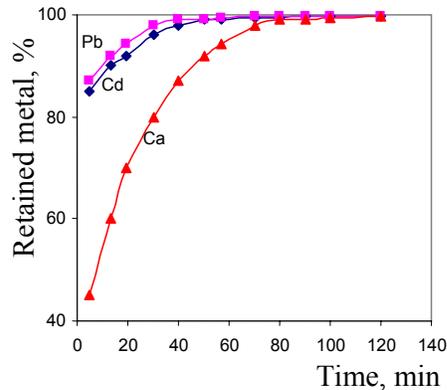


Fig. 1 – The sorption Cd(II), Pb(II) and Ca(II) on Chelex 100 (batch procedure)  
Cd(II) – 2.5 ppb, Pb(II) – 5 ppb, Ca(II) – 1 ppm; Chelex 100 – 0.6402 g;  
volume of solution – 25 mL.

The sorption could take place through complexation, by forming only one complex in the resin phase, or more than one complex and in this case more than one sorption mechanism has to be considered. There were determined from the correlation of the degree of adsorbed metallic ion on the resin vs. pH (Fig. 2). The pH value at which the sorption efficiency is 98-99% for cadmium and lead is 3.5 - 4 and at this pH value only 8 - 10% of calcium present in solution is retained.

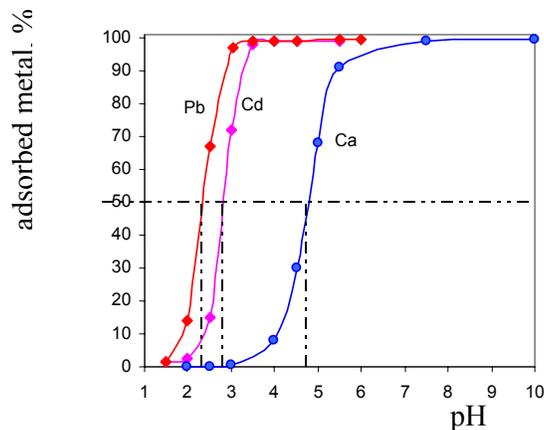


Fig. 2 – The effect of pH on metal sorption on Chelex 100  
Cd(II) – 2.5 ppb, Pb(II) – 5 ppb, Ca(II) – 1 ppm; Chelex 100 – 0.5892 g;  
volume of solution – 25 mL vs. pH.

The pH value is an important factor influencing the adsorption behaviour of metal ions on Chelex 100. Further investigation and the coordination mechanism seem to be necessary for a better understanding of the property.

It could be observed from Fig.3 that Cd<sup>2+</sup> and Pb<sup>2+</sup> are better adsorbed at a pH value between 2.5-3 and Ca<sup>2+</sup> at a pH value 4.5 - 5.

The optimal concentration of nitric acid used in the elution of the cations retained on the resin. For establishing this concentration, the percentage of eluted cation vs. concentration of nitric acid was represented. Results are shown in Fig. 4 and Fig. 5, determined by batch and elution methods.

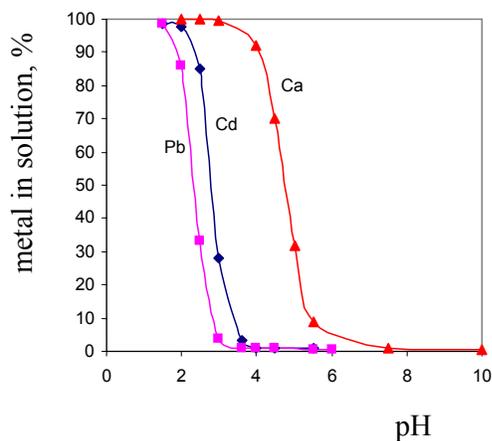


Fig. 3 – The efficiency of sorption on Chelex 100 vs. pH: Cd(II) – 2.5 ppb, Pb(II) – 5 ppb, Ca(II) – 1 ppm; Chelex 100 – 0.5892 g; volume of solution – 25 mL.

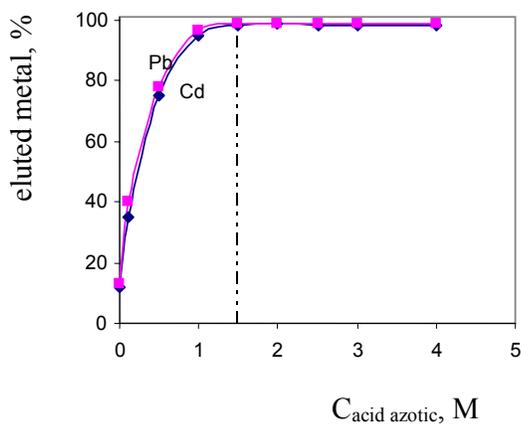


Fig. 4 – Influence of the concentration of nitric acid over the desorption Cd(II) – 2.5 ppb, Pb (II) – 5 ppb, Ca(II) – 1 ppm; Chelex 100 – 0.5892 g; volume of solution – 25 mL, batch method.

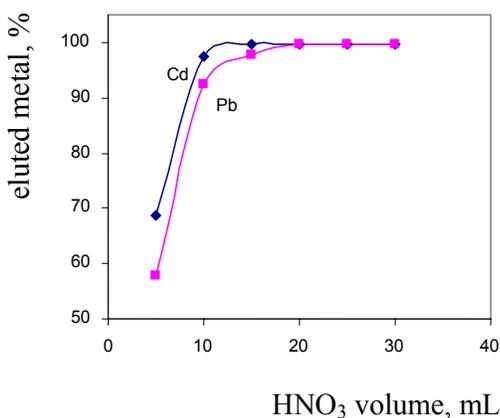


Fig. 5 – The influence of the volume of nitric acid over the elution of cationic species Cd(II) – 2.5 ppb Pb(II) – 5 ppb; HNO<sub>3</sub> – 1.5 M; Chelex 100 – 0.6261 g.

In order to release heavy metals pre concentrated on the sorbents, 1.5M HNO<sub>3</sub> was used. The minimum volume sufficient for a complete recovery of both Cd(II) and Pb(II) was 20 mL (Fig. 5). After the elution

step, the resin needs to be prepared for the next sample enrichment, by passing 10 bed volumes of 0.1 M HCl. Then the resin is washed with bi distilled waters to neutrality.

The separation of Cd(II) and Pb(II) adsorbed on Chelex 100 was examined through cartridge procedure, too, using 8 mL Altech tubes for solid phase extraction in which different amounts of resin were introduced and an Air Cadet – Altech vacuum pump for adjusting the flowing rates.

The effect of flow rate in cartridge preconcentration. Different flow rates were controlled by Air Cadet Pump in order to separate Cd<sup>2+</sup> and Pb<sup>2+</sup> from synthetic solution.

Cd<sup>2+</sup> and Pb<sup>2+</sup> concentrations in synthetic solutions<sup>27</sup> are the same with these in fertilizers. The results revealed that the flow rate variation in the range of 1 – 3 mL /min had no significant effect on the recovery of Cd(II) and Pb(II). It could be observed from Fig. 6 that the yields decreased under 90% for flow rates bigger than 3 mL.min<sup>-1</sup>.

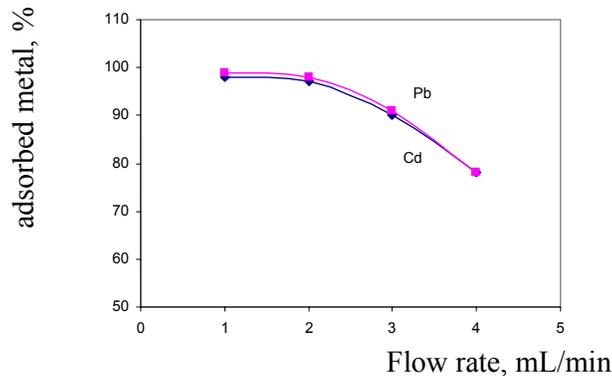


Fig. 6 – The influence of the flow rate over the sorption of Cd (II) – 2.5 ppb and Pb (II) – 5 ppb; HNO<sub>3</sub> – 1.5 M on Chelex 100 – 0.4632 g.

The effect of the eluent volume over the recovery of the metals in cartridge preconcentration. For establishing the optimum volume for a complete elution from the resin, there were used different volumes of 1.5M HNO<sub>3</sub> between 0.5 mL and 5 mL, resulting a 2 mL volume of 1.5M HNO<sub>3</sub> for a complete recovery using the cartridge procedure. In comparison with the batch procedure, this volume is smaller (2.5 mL in comparison with 20 mL), this fact allowing better preconcentration factors (Fig. 7).

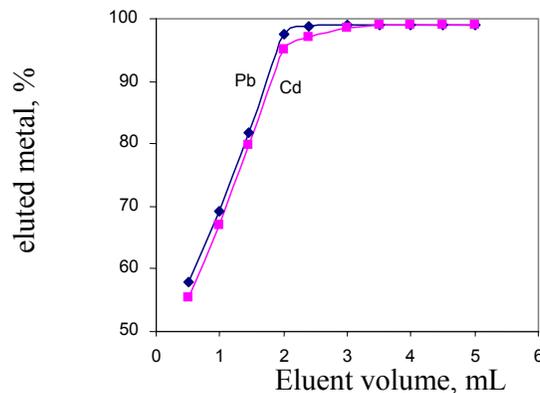


Fig. 7 – Influence of the volume of nitric acid over the elution of the cationic species from the resin.

Optimisation of the amount of resin in preconcentration step. Taking into account that in phosphate matrices there are several cations which can be retained on Chelex 100, for investigating the recovery yields for Cd(II) and Pb(II), synthetic solutions with similar matrices (three types of NPK fertilizers) were used for both procedures (batch and cartridge). For establishing the minimum amount of resin necessary in the pre-treatment of the samples, there were introduced different amounts of Chelex 100 in the cartridges (0.1 – 2.5 g), the

same volume of synthetic solution, using a similar procedure for all of them (flow rate -  $1 \text{ mL}\cdot\text{min}^{-1}$ , elution volume –  $5 \text{ mL } 1.5\text{M HNO}_3$ ). The recovery yields increased by increasing the amount of resin: 25% for 0.1 g, 80% for 0.5 g and 98-100% for amounts bigger than 1.5 g. In the cartridges 2g of Chelex 100 were introduced (Fig. 8).

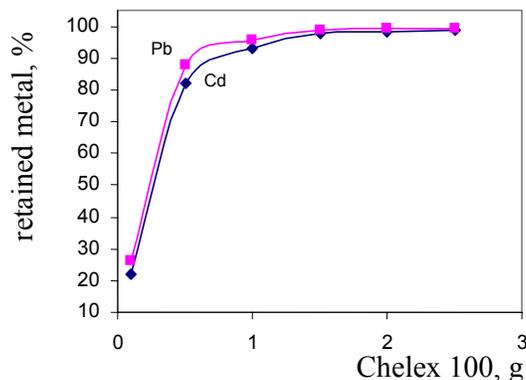


Fig. 8 – Optimization of the amount of resin used in the cartridge procedure.

For establishing the minimum amount of resin necessary for the pretreatment of the samples in the batch procedure, different amounts of Chelex 100 (0.1 g – 1 g) were used and the same volum of synthetic solution; all the samples were treated using the same procedure (contact time – 60 min, elution volume –  $20 \text{ mL } 1.5\text{M HNO}_3$ ). The recovery yields increased by increasing the amount of resin: 55% for 0.1 g, 70% for 0.2 g and 98-100% for amounts bigger than 0.4 g. In the batch procedure, 0.5 g of Chelex 100 were used (Fig. 9).

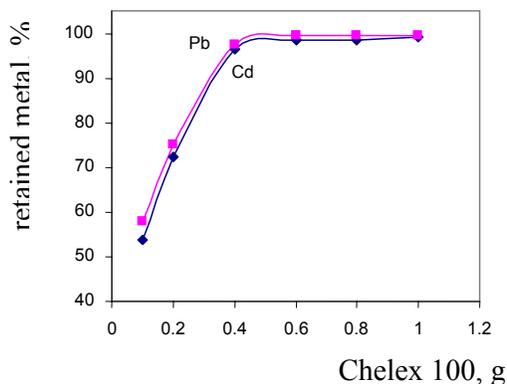


Fig. 9 – Optimization of the amount of resin used in the batch procedure: Cd(II) – 2.5 ppb, Pb(II) – 5 ppb.

In comparison with the cartridge procedure, which is faster and offers better concentration factors, in the batch procedure the necessary amount of resin are much more reduced, because of the bigger contact times.

Effect of interfering ions on the recovery of metal ions. In order to evaluate the possibility of selective recovery of Cd(II) and Pb(II) ions in the presence of some interferences, the determinations were done in a 1000- fold excesses of calcium, magnesium, sodium, potassium and a 500-fold excesses of aluminium and iron. The results showed little interference with the recovery of the tested metal ions. Cadmium and lead are quantitatively adsorbed on Chelex 100 in the pH range 4–7 and a excesses of mentioned cations do not affect the separation.

Application. The method was applied in the determination of cadmium and lead in some NPK fertilizers. Cadmium and lead were determined by AAS after preconcentration and the results obtained are presented in Table 1.

Table 1  
Cadmium and lead content (ppm) determined in different NPK fertilizers

Fertilizer	Metal ions (ppm)					
	Cd(II)	Recovery %	RSD* %	Pb(II)	Recovery %	RSD* %
NPK 10-30-10	21.1	98.2	0.8	15.61	97.3	1.3
NPK 10-40-20	20.6	97.7	0.9	6.42	97.5	1.3
NPK 10-40-10	17.27	97.0	1.2	3.2	97.0	1.5

\*Relative standard deviation was calculated for an average of six determinations.

## CONCLUSIONS

When metal ions are sorbed on Chelex 100 from aqueous solutions, the chelating mechanism with iminodiacetate clearly prevails if strong complexes are formed, while complexation by carboxylate prevails when metal ions with lower complexation constants with the iminodiacetate (Cd(II), Ca(II)) are involved.

The application of Chelex 100 resin used in this study has been shown to provide a convenient way for preconcentration of Cd(II) and Pb(II) in certain phosphate matrices, eliminating in the same time the interfering effect of phosphate ion and Ca(II) from the matrix.

The optimum conditions for the preconcentration step of heavy metals (Cd(II) and Pb(II)) from phosphate matrices on Chelex 100 are established.

This preliminary study will be continued for determination of heavy metals by AAS after preconcentration in other phosphate samples, phosphoric acid and fertilizers.

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