

## Articles

### Anodic Stripping Differential Pulse Voltammetric Determination of Trace Amounts of Lead after Preconcentration of Its Complex with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol onto Natural Analcime Zeolite by Column Method

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This work assesses the potential of natural Analcime Zeolite as an adsorbent for preconcentration of lead (II) traces. Lead is quantitatively retained on 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol by column method with Analcime in the pH range of 5-6.5 and 2 mL min<sup>-1</sup> flow rate. Lead was removed from the column with 10.0 mL of 4 M hydrochloric acid and was determined by anodic stripping differential pulse voltammetry. 0.5 ppb detection limit was obtained and linear dynamic range was 3 to 1.2 × 10<sup>5</sup> ppb in final solution with correlation coefficient of 0.999 and relative standard deviation of ± 1.2% (for eight replicate determination of 2.5 μg mL<sup>-1</sup> of lead). Various parameters such as the effect of pH, flow rate, instrumental conditions and interferences of some ions on the determination of lead have been studied in detail for optimization of conditions. The method was successfully applied for determination of lead in various samples.

**Key Words :** Lead determination, Preconcentration, Zeolites, Stripping voltammetry

#### Introduction

Trace analysis of heavy metals is an important part of studies in analytical chemistry. Determination of these ions in various materials from industrial samples to environmental samples has been performed continuously.<sup>1</sup> The most common technique available for preconcentration of metals from aqueous samples is solvent extraction and solid-phase extraction using various adsorbents such as thiol cotton,<sup>2</sup> activated carbon,<sup>3</sup> green tea leaves,<sup>4</sup> adsorption resins,<sup>5</sup> cellulose,<sup>6</sup> polythioether,<sup>7</sup> microcrystalline naphthalene,<sup>8-10</sup> Amberlite XAD-2 resin,<sup>11</sup> octadecylsilica membrane disk<sup>12</sup> and synthetic Zeolites.<sup>13</sup> Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their preparations are lengthy and control of conditions is rigid.

Zeolites are highly crystalline aluminosilicate with [SiO<sub>4</sub>]<sup>4-</sup> and [AlO<sub>4</sub>]<sup>5-</sup> tetrahedral units as frameworks. An oxygen bridge joins Si and Al atoms. Counter ions such as Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> are required for neutralization of overall negative surface charge. Due to the charged nature of the framework and its ability to form Bronsted acid sites, Zeolites are useful catalyst for many applications.<sup>14</sup> Zeolites have been used in purification processes like gas sweetening and air decontamination as well as in separation processes<sup>15</sup> and it is believed that the attitude is attributed to the adsorption of cationic surfactants onto Zeolite surface.<sup>16</sup> The potential of synthetic Zeolites for the enrichment of metallic

traces has been investigated.<sup>13</sup> Nevertheless, the potential of natural Analcime Zeolite as useful material for the enrichment of metallic traces has not been investigated yet.

Earlier, much attention was given to direct polarographic estimation of metals after extraction of their metal complexes into organic solvents.<sup>17-21</sup> Unfortunately, electrochemical methods for direct determination of reducible substances, requires that the solvent should have a fairly high dielectric constant so as well-defined polarogram can be obtained. In this regard, various workers have mixed the organic phase after extraction with a solvent of high dielectric constant to obtain well-defined polarograms.<sup>22</sup> The main disadvantage of these methods is that the sensitivity and preconcentration factors are considerably lowered. Thus, the aim of preconcentration and direct determination of metal is not achieved. Among the polarographic and voltammetric methods, anodic stripping voltammetry<sup>23,24</sup> and anodic stripping differential pulse voltammetry<sup>25</sup> are fairly sensitive. The preconcentration step not only improves the selectivity of a method but also enhances its application for determination trace amount of metal ions from a large volume sample, whereas with direct differential pulse polarography, it is not possible.<sup>26</sup> The purpose of this study is to investigate for the first time, the analytical potential of natural Analcime Zeolite as sorbent material for preconcentration of lead traces by formation of complex. In the present work, we have developed a simple, sensitive and economical method for anodic stripping differential pulse voltammetric determination of lead (II) after adsorption of its 2-(5-bromo-2-pyridalzo)-5-diethylaminophenol (5-Br-PADAP) as it is

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the metal complex which is adsorbed onto natural Analcime Zeolite and subsequent desorption by 10.0 mL of 4 M hydrochloric acid, and HCl itself acts as a supporting electrolyte. The selected reagent 5-Br-PADAP does not interfere with voltammetric estimation of lead ion and most of the problems with above mention voltammetric methods are solved by this method. The method is found to be highly selective, rapid, economical and sensitive. The developed procedure has been used for determination of lead in various samples.

### Experimental Section

**Apparatus.** Voltammograms were recorded with a three electrode system. A polarograph 757 VA computrace (Metrohm) was used for anodic stripping differential pulse voltammetry at the hanging mercury drope electrode (HMDE). A funnel tipped glass tube (80 × 10 mm) was used as a column for preconcentration. The laboratory glassware and columns were kept overnight in a mixture of concentrated sulfuric and nitric acid (1 : 1). A Corning 140 pH meter was used for pH measurements.

**Reagents.** All chemicals used were in analytical reagent grades. Lead(II) nitrate was dissolved in double distilled water and diluted to 1000 mL in a standard flask and standardized by known methods.<sup>27</sup> Buffer solution of pH 3-6.5 were prepared by mixing an appropriate ratio of 0.5 M acetic acid and 0.5 M sodium acetate. A 0.02% solution of 5-Br-PADAP in ethanol was prepared. Solution of various metals were used to study the interference of ions. Natural Analcime Zeolite was collected from Torfeh, Shahr Babak area, Kerman region in Iran.<sup>28</sup>

**Preparation of the Analcime Zeolite.** After purification of Analcime,<sup>29</sup> the Zeolite was sieved to obtain a particle size of <150 μm (200 mesh) and 4 M hydrochloric acid was added to Zeolite and then washed with distilled water until it was neutral pH, then the adsorbent in this form dried at 110 °C in an oven and stored in a calcium chloride desiccator until used.

**Procedure for the sorption of lead on the column.** 1 g of the Analcime Zeolite was added to a funnel tipped glass tube and 3 mL of buffer with pH ~5.5 passed from the column. An aliquot of the solution containing 0.03-1200 μg of lead was taken in a 100 mL beaker and 5 mL of 0.02% alcoholic solution of 5-Br-PADAP and 5 mL of buffer (pH ~5.5) added to it then, diluted to ~50 mL with distilled water. This solution then passed through the column at a flow rate of 2 mL min<sup>-1</sup>. After passing this solution, the column was eluted with 5 mL of distilled water. The adsorbed lead on the column was eluted with 10.0 mL of 4 M hydrochloric acid solution at a flow rate of 1 mL min<sup>-1</sup>. The eluent was collected in a 10.0 mL volumetric flask and lead was determined by anodic stripping differential pulse voltammetry.

The sorption capacity of natural Analcime Zeolite for the lead complex with 5-Br-PADAP was also evaluated. The natural Analcime Zeolite has a sorption capacity of 1.65 mg of lead per gram of Analcime.

**Table 1.** Analysis of lead in standard alloys

Sample	Composition %	Found*
NKK No. 916 Aluminum Alloy	Si, 0.41; C, 0.41; Fe, 0.54; Mg, 0.1; Cr, 0.05; Sn, 0.05; Zn, 0.3; Ti, 0.1; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Co, 0.03; Mn, 0.11; Bi, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27	0.039 ± 0.003
NKK No. 1021 Al, Si, Cu, Zn Alloy	Pb, 0.18; Zn, 1.76; Si, 5.56; Sn, 0.10; Mg, 0.29; Ti, 0.04; Cr, 0.03; Fe, 0.99; Bi, 0.01; Zr, 0.01; Sb, 0.01; Ca, 0.004; Mn, 0.20; Ni, 0.14; V, 0.007; Cu, 2.72	0.175 ± 0.002
NKK No. 920 Aluminum Alloy	Cr, 0.27; Si, 0.78; Bi, 0.06; Ti, 0.15; Sn, 0.20; Ga, 0.05; Pb, 0.10; Fe, 0.72; Zn, 0.80; Ca, 0.03; Mg, 0.46; Sb, 0.10; Co, 0.10; Mn, 0.20; Ni, 0.29; V, 0.15; Cu, 0.71	0.097 ± 0.004

\*Average of five determinations, ± standard deviation, Conditions: Reagent, 5 mL 0.02% of 5-Br-PADAP; buffer, 5 mL; flow rate of sample, 2 mL min<sup>-1</sup>; final solution, 10.0 mL of 4 M HCl solution; reference, reagent blank; Instrumental setting: deposition time, 120 s; deposition potential, -0.80 V; pulse amplitude, 0.05 V; pulse time, 0.4 s; scan rate, 15 mV s<sup>-1</sup>; purge time, 300 s.

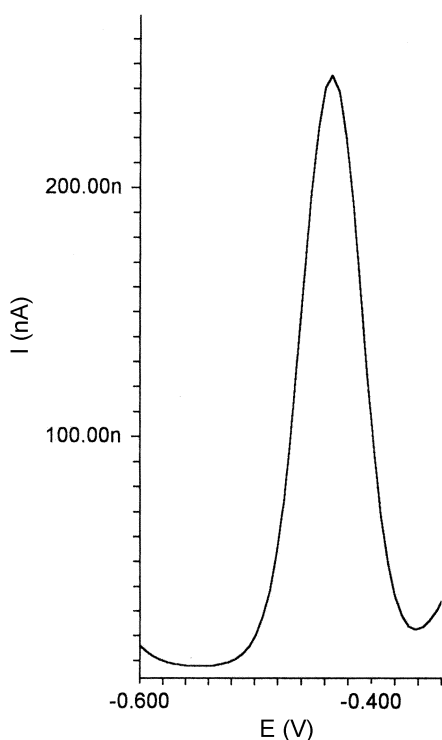
**Determination of lead in standard alloys.** The method was applied for determination of lead in Nippon Keikin-zoku Kogyo (NKK) CRM, No. 916 and No. 920 Aluminum Alloy, NKK No. 1021 Al, Si, Ca, Zn, Alloy. A 0.10 gram sample of the standard alloy was dissolved completely in 10 mL hydrochloric acid (1+1) by heating on a water-bath and then 1 mL of 30% (v/v) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on a water-bath. The solution was cooled, filtered and diluted to 100 mL with distilled water in a standard flask. An aliquot (5.0 mL) of this sample was taken in a 20 mL beaker and the general procedure was applied. The results obtained are given in Table 1. These results are in agreement with certified values and cleared the proposed method have good accuracy.

**Analysis of lead in natural waters, tea leaves and human hair.** The method has been employed for the determination of lead in cities water, well water, river water

**Table 2.** Analysis of lead in natural waters

Sample/water	Lead found* (ppb) by AAS	Lead found** (ppb) by present method
Kerman drinking water	31.3 ± 1.3 <sup>a</sup>	31 ± 2
Well water	—	82 ± 3
Shiraz drinking water	—	27 ± 1
Rayen drinking water	27.9 ± 1.2 <sup>a</sup>	28 ± 1
Sirjan drinking water	—	39 ± 2
River water	12.3 ± 1.1 <sup>b</sup>	12 ± 1
Spring water	14.9 ± 1.5 <sup>b</sup>	15 ± 1

\*After preconcentration of lead by present method and determination by atomic absorption spectrometry, ± standard deviation, \*\*Average of five determinations, <sup>a</sup>Determination by flame atomic absorption spectrometry, <sup>b</sup>Determination by graphite furnace atomic absorption spectrometry. Conditions and instrumental setting were same as Table 1.



**Figure 1.** A voltammogram for lead in spring water in final solution after extraction and preconcentration. Conditions: Reagent, 5 mL 0.02% of 5-Br-PADAP; buffer, 5 mL; flow rate of sample, 2 mL min<sup>-1</sup>; final solution, 10.0 mL of 4 M HCl solution; reference, reagent blank; Instrumental setting: deposition time, 120 s; deposition potential, -0.80 V; pulse amplitude, 0.05 V; pulse time, 0.4 s; scan rate, 15 mV s<sup>-1</sup>; purge time, 300 s.

and spring water. A 50 mL water sample was adjusted to pH = 1 with nitric acid, filtered and analyzed by general procedure. The results are given in Table 2 and a voltammogram for spring water was shown in Figure 1. The results was compared by atomic absorption spectrometry that shown in Table 2. In this case, the general procedure for extraction and preconcentration was applied and lead ion in final solution was determined by flame or graphite furnace atomic absorption spectrometry.

The method applied for determination of lead in tea leaves. The tea leaves were dried in an oven at 110 °C for 12 h, then 1.0 g of the sample was decomposed with 6 M of hydrochloric acid and 4 mL of 30% hydrogen peroxide was added. The mixture was heated on a water - bath until dried, then 20 mL distilled water was added to it and filtered. The solution was diluted to 100 mL with distilled water in a standard flask. An aliquot (10 mL) of this sample was taken

**Table 3.** Analysis of lead in tea leaves and human hair

Sample	Found* (ppm)
Tea leaves (sample 1)	2.25 ± 0.08
Tea leaves (sample 2)	14.7 ± 0.4
Human hair (male)	6.2 ± 0.1

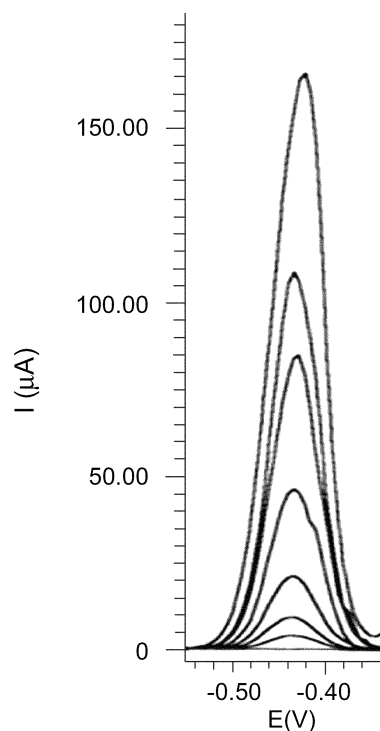
\*Average of five determinations, ± standard deviation, Conditions and instrumental setting were same as Table 1.

in a 20 mL beaker and general procedure was applied. The results obtained are given in Table 3.

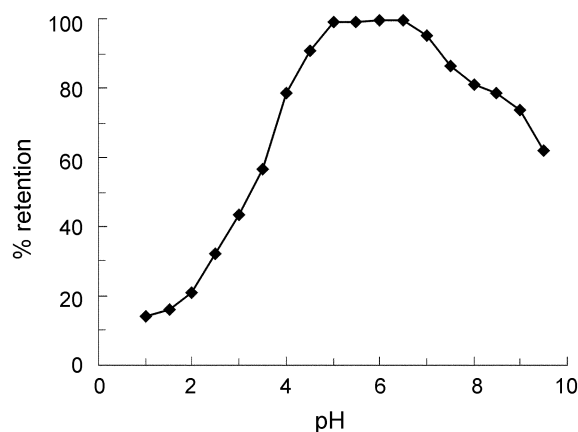
The method was applied for determination of lead in human hair, a 10.0 g sample was decomposed by 30 mL of concentrated nitric acid and 5 mL of 50% perchloric acid, then the solution heated until dried. Then, distilled water added to it, filtered and diluted to 200 mL in a calibrated flask. An aliquot of this solution was taken through the general procedure. The results obtained in Table 3.

## Results and Discussion

**Anodic stripping differential pulse voltammetry.** In order to determine the optimum conditions for quantitative extraction of lead by using Analcime with 5-Br-PADAP complex, several parameters were assessed. In the present work, the differential pulse voltammogram for lead was obtained in HCl medium as supporting electrolyte. A sample solution was transferred into the voltammetric cell, after the removal of dissolved oxygen by passing purified nitrogen gas for 5 minutes, the voltammograms were recorded by sweeping the potential from -0.6 to -0.3 V versus Ag/AgCl reference electrode (Fig. 2). The half-wave potential was -0.44 V. Lead was deposited on a hanging mercury drop electrode at -0.80 V for 120 s, while stirring the solution. The amalgamate lead was stripped by differential pulse voltammetry by scanning of the electrode between -0.60 and -0.30 V with scan rate of 15 mV s<sup>-1</sup> and pulse amplitude of 50 mV.

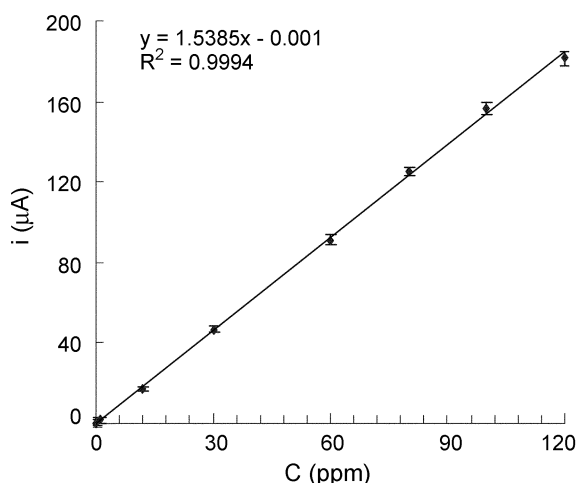


**Figure 2.** Anodic stripping differential pulse voltammograms of lead (II). Lead (II) concentration: 110, 70, 55, 30, 14, 5.0, 1.2 ppm and background response from up to down, respectively. Conditions and instrumental setting were same as Fig. 1.

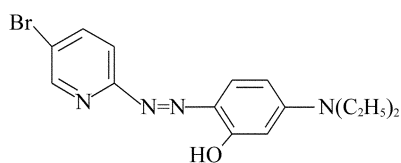


**Figure 3.** Effect of pH on adsorption of lead complex. Lead, 25  $\mu\text{g}$  in 10.0 mL final 4 M HCl solution. Conditions and instrumental setting were same as Fig. 1.

**Reaction conditions.** The reaction conditions were investigated with 25  $\mu\text{g}$  of lead. The sorption of lead on the column was found maximum in the pH range of 5-6.5 (Fig. 3). In subsequent studies, the pH was maintained at  $\sim 5.5$ . The flow rates was varied from 0.2-5  $\text{mL min}^{-1}$ . It was found that a flow rate of 0.2-4  $\text{mL min}^{-1}$  did not affect adsorption. A flow rate of 2  $\text{mL min}^{-1}$  was recommended in all experiments. The volume of the aqueous phase was varied in the range 50-1000 mL under the optimum conditions, keeping the other variable of constant. It was observed that the current height was almost constant up to 500 mL (pre-



**Figure 4.** Calibration curve for lead (II). Conditions and instrumental setting were same as Fig. 2.



**Figure 5.** Structure reagent of 5-Br-PADAP.

**Table 4.** Effect of diver ions on the lead determination<sup>a</sup>

Salt or ion	Tolerance limit
$\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$	2 g
$\text{KNO}_3$	1 g
$\text{NaCl}$ , $\text{NaF}$	100 mg
$\text{NH}_4\text{Cl}$	50 mg
$\text{NH}_4\text{SCN}$	200 mg
$\text{Na}_2\text{EDTA}$	95 $\mu\text{g}$
Sodium oxalate, $\text{Na}_2\text{S}_2\text{O}_3$	90 mg
Zn (II)	7.0 mg
Mn (II)	5.0 mg
Al (II)	30 mg
V (V)	10 mg
Fe (III)	50 $\mu\text{g}$ , 1.0 $\text{mg}^b$
Bi (III)	15 mg
As (III)	12 mg
Co (II)	4.0 mg
Hg (II), Ni (II)	5.0 mg
Zn (II)	2.5 mg
Cu (II)	2.0 mg
Cd (II)	0.8 mg
Tl (I)	6.0 mg
Pd (II), Te(IV)	6.5 mg

<sup>a</sup>Conditions: Lead, 25  $\mu\text{g}$  in 10.0 mL final 4 M HCl solution; buffer, 5 mL; reagent, 5 mL 0.02% of 5-Br-PADAP; flow rate of sample, 2  $\text{mL min}^{-1}$ ; final solution, 10.0 mL of 4 M HCl solution; reference, reagent blank; Instrumental setting: deposition time, 120 s; deposition potential, -0.80 V; pulse amplitude, 0.05 V; pulse time, 0.4 s; scan rate, 15  $\text{mV s}^{-1}$ ; purge time, 300 s. <sup>b</sup>Masked with 2 mL of 5% NaF solution,

concentration factor of 50). However, for convenience, all experiments were carried out with 50 mL of aqueous phase.

Lead was desorbed completely with 10.0 mL of 4 M hydrochloric acid, therefore 10.0 mL of 4 M hydrochloric acid, was used in the present work.

**Calibration and sensitivity.** A calibration plot for the determination of lead was prepared according to the general procedure under the optimum conditions developed above from its anodic stripping differential pulse voltammogram with different concentrations. A typical voltammogram for lead is given in Figure 2. Since it is possible to retain 5 ng of lead from 500 mL of solution with passing through the column and desorption with 10.0 mL hydrochloric acid gives a detection limit of 0.01 ppb for lead in first solution. The linear range was maintained in the concentration range of 3 to  $1.2 \times 10^5$  ppb lead in final aqueous solution with a correlation factor of 0.999 (Fig. 4). Eight replicate determination of 25  $\mu\text{g}$  of lead in 10.0 mL hydrochloric acid solution gave a mean current of 3.83  $\mu\text{A}$  with a relative standard deviation of  $\pm 1.2\%$ .

**Effect of foreign ions.** Various salts and metal ions were added individually to a solution containing 25  $\mu\text{g}$  of lead and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ion required to cause  $\pm 3\%$  error in the determination of lead(II). The tolerance limit (error  $< 3\%$ ) is given in Table 4. Among the salts and metal ions examined, most of them did not interfere at the

gram or milligram level except  $\text{Fe}^{3+}$ , and it was masked with 2 mL of 5% NaF solution. Thus, the method is selective and the proposed procedure has been applied for determination of lead in samples.

### Conclusion

It is difficult to obtain a well-defined voltammogram in the traditional analysis for metal ions because the concentration is low, therefore, preconcentration is necessary. The main advantages of this procedure are: (I) natural Analcime is very cheap; (II) the preparation of extractor system is simple and fast; (III) the eluent solution (hydrochloric acid) is cheap; (IV) eluent hydrochloric acid acts as supporting electrolyte; (V) good preconcentration factor can be achieved, (VI) the 5-Br-PADAP reagent is fairly sensitive and selective for lead (Fig. 5), (VII) installation of this procedure is simple and low cost. The proposed procedure has been applied for lead determination in various samples.

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