Determination of lead in environmental samples after solid phase extraction by 2-aminothiazole group incorporated PS-DVB

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Proposed method for determination of trace amounts of lead is based on solid phase extraction of metal ion by 2-aminothiazole group incorporated into a matrix of polystyrene-divinylbenzene (PS-DVB). Effect of pH, equilibration rate, sorption and desorption of metal ions, effect of flow rate and effect of diverse ions were studied. Maximum sorption capacity observed for Pb (II) was 0.29 mmolg⁻¹ at pH 5.5. Calibration range was linear up to 5 µg ml⁻¹ (R²=0.997) with a detection limit of 25.0 µg l⁻¹. Pb (II) recovery at 97.5% confidence level was found to be 97.5 ± 2.1%.

Keywords: Pb (II), 2-Aminothiazole, Microwave-assisted dissolution, Solid phase extraction

Introduction
Presence of even traces of Pb (II) in environmental samples leads to environmental pollution and many fatal diseases including dysfunction of renal blood and neurological systems¹. Pb (II) easily deposits in blood, kidney, reproductive system, nervous system and brain, and its acute exposure can result in colic shock, severe anemia and irreversible brain damage². Lead compounds as antiknocking agent in automobile fuel cause air pollution.

Spectrophotometric methods for determination of lead are reported³⁵ to face interference due to the presence of several metal ions. Flame atomic absorption spectrometry (FAAS) is used in determination of lead traces. Solid phase extraction (SPE) used for determination of Pb (II) includes solid supports like 2-aminothiophenyl-S-acetic acid anchored on chloromethyl polystyrene⁶, dithiooxamide on chloromethyl polystyrene⁷, 8-hydroxyquinoline on cellulose⁸, resacethophenone on silica gel⁹, o-aminophenol on Amberlite XAD-2¹⁰, o-aminobenzoic acid on XAD-4¹¹, zirconium phosphate on silica gel¹², pyrochatechol violet on Amberlite XAD-2¹³ and quinalizarin on Amberlite XAD-2¹⁴. Chelating resin with 2-aminothiazole group has been synthesized and used¹⁵ to separate cadmium and mercury from biological samples.

Present study proposes a simple and efficient method for determination of lead by FAAS.

Materials and Methods
Materials
FAAS measurements were carried out with a GBC AVANTA Atomic Absorption Spectrometer (model 908 BT) with lamp by setting current (3 mA) and wavelength (283.3 nm) for lead. Systronic digital pH meter (model 335) was used for pH adjustments. A domestic Samsung microwave oven (model CE2933) with a 2450 MHz frequency magnetron and 900 W maximum power and a polytetrafluoroethylene (PTFE) reactor (115 ml internal volume, 1 cm cell wall thickness and hermetic screw caps) were used for digestion.

Stock solution of Pb (II) was obtained from E. Merck (Germany). Working solutions were prepared by appropriate dilution with deionised water. All other chemicals were of reagent grade. Glass apparatus were soaked in 4 M HNO₃ overnight and cleaned with double distilled water. Reference materials analyzed were: standard reference materials (SRM) 1573 tomato leaves from National Bureau of Standards; pond sediment (NIES 2); and igneous rock (JR-1) from National Institute for Environmental Studies, Japan.
Analytical Procedure

For dissolution, samples (100-150 mg) were treated in a hermetically sealed PTFE (15 ml) reactor in sequence (450 W, 2.5 min each) with 1.5 ml of hydrofluoric acid (HF), 4 ml of aqua regia and 3 ml of H$_2$O$_2$. The digested sample was boiled with saturated boric acid (5 ml) for 10 min in a water bath to remove excess HF. Road dust samples, collected from different places on G T Road, Burdwan (West Bengal, India), were also digested as above.

Metal ion capacity of 2-aminothiazole was determined for Pb (II) by using batch technique. A measured excess of metal ion solution was added to 2-aminothiazole resin (50 mg) taken in a conical flask (50 ml). pH (1.0-5.5) of the solution was adjusted by adding 0.1 M HCl or 0.2 M sodium acetate solution. Residual Pb (II) was determined by FAAS using an air–acetylene flame. Resin thus obtained was shaken with 30 ml of various eluants (0.01 M-2 M HCl and HNO$_3$) for 24 h and filtered. The concentration of Pb (II) was determined in the filtrate by FAAS.

Air-dried resin (1.5 g) was immersed in double distilled water and allowed to swell for 24 h. A glass column (130 mm x 10 mm) was packed with swollen beads to a bed volume of 2 ml. Sorption and desorption characteristics for Pb (II) in the column were studied at the flow rate of 0.5 ml min$^{-1}$. Sorbed Pb (II) was eluted completely with 2 M HNO$_3$.

Results and Discussion

Sorption and Desorption of Metal Ions

Sorption capacity of Pb (II) on 2-aminothiazole resin as a function of pH was determined by batch method (Fig. 1). Maximum capacity for Pb (II) at pH 5.5 is 0.29 mmol g$^{-1}$. 2 M HNO$_3$ showed maximum desorption of lead (Fig. 2).

Effect of Diverse Ion and Separation of Pb (II) from Spiked Binary Mixtures

Separation of lead (2 µg ml$^{-1}$) from binary mixtures in a sample (50 ml) at pH 5.5 by foreign ions (added at 2000 µg ml$^{-1}$ level) has been found as follows: Na (I), Ca (II) and Mg (II), 100; Ni (II), 98.4; Mn (II), 98.2; Ag (I), 97.8; Cu (II) 96.8; Sn (II), 96.7; and Cd (II) 93.4%. Presence of diverse metal ions (alkali, alkaline earth and first transition series including Cd and Ag) did not interfere in the sorption step. Pb (II) was eluted with 2 M HNO$_3$ and concentration was measured by FAAS. Results show that entire Pb (II) can be recovered from binary mixtures.

Equilibration Rate and Effect of Flow Rate of Sample Solution

Uptake (50%) of Pb (II) required 22 min. Thus, resin is suitable for column operation under a low flow rate (0.1-0.5 ml min$^{-1}$). Flow rate of sample solution affects retention of Pb (II) on the resin. Under optimum conditions of pH and eluant, flow rate (0.1-0.6 ml min$^{-1}$) gave (Fig. 3) optimum retention of Pb (II). In present work, 0.5 ml min$^{-1}$ was chosen as optimum flow rate.

Analytical Figures-of-Merit

Concentration range for calibration curve was linear up to 5 µg ml$^{-1}$ for Pb (II) with a regression coefficient ($R^2$) of 0.997. Detection limit (3σ of the blank signal) was found to be 25.0 µg l$^{-1}$ for Pb (II) using spiked sample solutions. Precision of the method was evaluated by successive retention and elution cycle with 0.1 g of Pb (II) in 100 ml of solution. Recovery was 97.5 ± 2.1 % for Pb (II) at 97.5% confidence level.
Table 1—Determination of Pb (II) in certified environmental samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Certified values, µg g⁻¹</th>
<th>Value obtained*, µg g⁻¹</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tomato leaves, 112 mg</td>
<td>6.3 ± 0.3</td>
<td>6.0 ± 1.2</td>
<td>-4.8</td>
</tr>
<tr>
<td>Pond sediment, 100 mg</td>
<td>105 ± 6</td>
<td>100 ± 7.8</td>
<td>-4.8</td>
</tr>
<tr>
<td>Igneous rocks, 114 mg</td>
<td>19.1</td>
<td>17.8 ± 1.2</td>
<td>-6.8</td>
</tr>
</tbody>
</table>

*Average of 5 determinations

Table 2—Comparison of exchange capacity of different chelating resins

<table>
<thead>
<tr>
<th>Active functional group</th>
<th>Exchange capacity of Pb (II), mmol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Aminothiophenyl-S-acetic acid⁶</td>
<td>0.03</td>
</tr>
<tr>
<td>Dithiooxamide⁷</td>
<td>0.12</td>
</tr>
<tr>
<td>8-Hydroxyquinoline⁴</td>
<td>0.094</td>
</tr>
<tr>
<td>Resacetophenone⁹</td>
<td>0.066</td>
</tr>
<tr>
<td>α-Aminophenol¹⁰</td>
<td>0.016</td>
</tr>
<tr>
<td>α-Aminobenzoic acid¹¹</td>
<td>0.059</td>
</tr>
<tr>
<td>Zirconium phosphate¹²</td>
<td>0.096</td>
</tr>
<tr>
<td>Pyrochatelin violet¹³</td>
<td>0.006</td>
</tr>
<tr>
<td>Quinalizarin¹⁴</td>
<td>0.025</td>
</tr>
<tr>
<td>Imidazolylazobenzene¹⁶</td>
<td>0.251</td>
</tr>
<tr>
<td>1,4-Bis(imidazolylazo)benzene¹⁶</td>
<td>0.287</td>
</tr>
</tbody>
</table>

Determination of Pb (II) in Different Certified Samples

Certified samples were digested in a microwave oven by the described analytical procedure. Pb (II) was separated using 2-aminothiazole resin and analyzed by FAAS. The values of amounts present in certified samples are similar to that found by the present method (Table 1).

Analysis of Pb (II) in Road Dust

Proposed procedure gave following values of Pb (II) in road dust from different stations: station 1, 45.9 ± 0.6; station 2, 126.4 ± 0.2; and station 3, 233.5 ± 0.4 µg g⁻¹.

Resin Exchange Capacity

Resin containing 2-aminothiazole group has been found to be very selective for Pb (II) at pH 5.5. Compared to the solid phase exchangers⁶-¹⁴,¹⁶ (Table 2), this resin shows highest exchange capacity, may be due to the presence of sulfur and nitrogen donor atoms. Thus, resin can be very effective in separation of Pb (II) from digestate of different environmental samples.

Conclusions

Using proposed method, entire Pb (II) can be recovered from binary mixtures at following conditions: pH, 5.5; eluant, 2 M HNO₃; and flow rate, 0.5 ml min⁻¹. Resin containing 2-aminothiazole showed highest exchange capacity as compared with other reported groups.

Acknowledgement

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References

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