

Determination of Lead by Flame Atomic Absorption Spectrometry after Pre-concentration using Silica Gel Coated with Schiff's Bases.

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Abstract

A method for pre-concentration of Pb(II) is proposed by using a minicolumn filled with silica gel modified by Schiff's base (N,N'-Bis(salicylidene)1,3-propylenediamine). The retained analyte on the prepared sorbent were eluted with a small amount of HNO₃. The metal ions in the eluent were determined by flame atomic absorption spectrometer (FAAS). Different factors, including the pH of the sample solution, the sample volume, and the amount of the Schiff's base were examined to optimize the conditions for the pre-concentration of these metal ions in aqueous solutions. The matrix effect of some different compounds has been also studied to know the separation efficiency of the sorbents. The concentration factors were up to 100.

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1. Introduction

Lead analysis is of prime interest because of its cumulative toxicity and harmful influences on animals and human health. 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 systems. 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 damage. Lead compounds as antiknocking agent in automobile fuel cause air pollution [1]. Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples. Additionally, since high levels of nontoxic components usually accompany analytes, a clean-up step is often required. In recent years, solid phase extraction (SPE) has been successfully used for the separation and sensitive determination of metal ions [2,3]. Solid phase extraction based on adsorption is a recently used method that compensates solvent extraction disadvantages. The solid phase extraction technique reduces organic solvent usage and exposure, disposal costs, and extraction time for sample preparation. Solid phase extraction allows adsorbing chemical species directly onto a solid phase as an adsorbent provides an effective separation. The relatively high concentration factor and the ability of treating large volume samples compared to the other separation-preconcentration techniques are other advantages of the solid phase extraction [4]. A number of sorbents have been widely used for the preconcentration and separation of trace metal ions from various matrices. Sorbents used in preconcentration systems for lead determination can be unloaded, loaded or chemically modified with the help of complexing reagents. Unloaded supports like activated carbon, natural adsorbents, amberlite XAD resins, polyethylene, and others are potential collectors of analytes in the form of a single ion or associated with other species such as complexes. The solid-phase extraction (SPE), provide dual advantages: an increase in analyte concentrations to measurable levels and the removal of potentially interfering matrices [5,6]. Schiff base compounds derived from salicylaldehyde (salens and salophens) as polydentate ligands are able to form stable complexes with several transition metal ions. These ligands have been applied as ionophore in construction of membrane electrodes, optical sensors, and as modifiers in solid phase extraction [7-10]. In this paper, a new separation/preconcentration method was described for the determination of Pb(II) in water samples by FAAS using silica gel loaded with Schiff's base.

2. Experimental

2.1. Apparatus

The absorption measurements were made with Shimadzu model AA-6200 atomic absorption spectrometer. The pH measurements were made by a Knick pH-Meter 761. A pre-concentration system from J.T. Baker has been used.

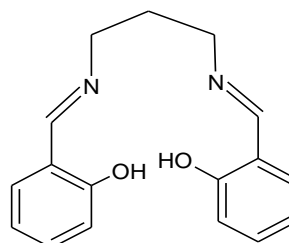
2.2. Reagents

All the reagents were of analytical reagent grade. Milli-Q water (deionized water) was used throughout.

The Lead standard solutions were prepared from a standard solution (1000mg/l) from Merck (Germany). Appropriate dilutions were made, whenever necessary, with deionized water

PS

N,N'-Bis(salicylidene)1,3-propylenediamine



2.3. Preparation of the column:

6ml columns filled with 1g silica gel each from J.T.Baker were used. 6ml of 10^{-2} M Schiff's base in acetone passed through the column by gravity action after cleaning with 3ml 2M HNO_3 , then 20ml MilliQ water, then 2ml methanol, and finally 2ml acetone. The columns have been kept at room temperature for approximately 30 minutes to complete the solvent evaporation.

2.4. General procedure for Pb determination

After adjustment of Pb sample solutions to pH 4-5, given volumes up to 1000ml of Pb(II) were passed through the column at flow rate of 4-10ml/min. After a washing step with 3ml deionized water the adsorbed metal was eluted with 10ml of 2mol/L HNO_3 at an elution rate of 10ml/min. The concentration of metal ions in the eluate was determined by FAAS.

3. Results and discussion

3.1. Effect of pH

Due to chemical sensitivity of functional groups of sorbent surface, the influence of pH value has to be carefully investigated. In this study, the pH values of the element solutions were adjusted within the range of 1-10 using HNO_3 or NH_4OH . As shown in figure (1) the optimum retention pH range of the sample solution was 3-5. The low recovery at lower pH can be associated with the protonation of functional groups of the sorbent and a low degree of swelling. At such a pH value, Pb(II) ions occur in a hydrated form $[\text{M}(\text{OH}_2)_n]^{2+}$ form. The swelling capacity grows with increase of pH of solution (pH 3-5), which favors the interaction between the metal ions and coordinatively active groups of the sorbent. Along with the hydrated cationic form, Lead in aqueous solutions at $\text{pH} > 5$ can occur in the form of $[\text{M}(\text{OH})(\text{OH}_2)_{n-1}]^+$ hydroxo complexes. At higher pH values, hydrolysis is accelerated and, as a consequence, the degree of Pb sorption is gradually reduced [11,12].

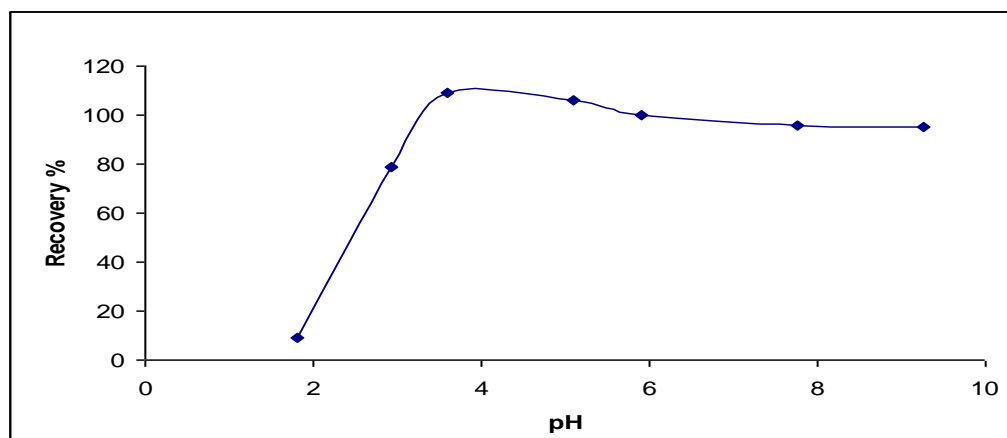


Figure 1: Influence of sample pH on the recovery of Pb(II) from silica gel coated with Schiff's bases ligand.

3.2. Effect of sample volume

Studies were also performed with Pb(II) solutions with different volumes to find the possibility to enrich solutions at low concentrations with a high concentration factor. A series of 50, 100, 250, 500 and 1000ml solutions spiked with $50\mu\text{g}$ of Pb have been tested (Fig.2). The recovery values were quantitative up to 1000ml, the highest pre-concentration factor was found to be 100.

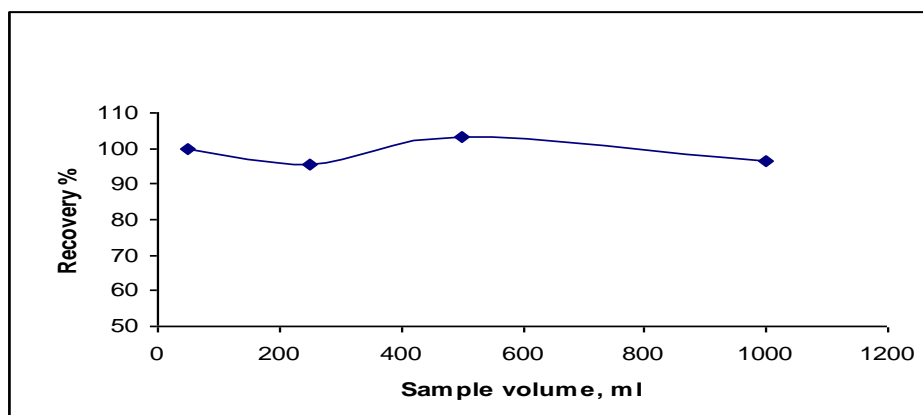


Figure 2: Influence of Schiff's base volume on the recovery of Pb(II) ion.

3.3. Interference effect

Various salts and metal ions with different charges and different atomic sizes were added individually to 50ml of solutions containing 50µg Pb (II), in different ratios (1:1), (1:10), and (1:100) and the general procedure was applied. The results obtained are presented in figure (3).

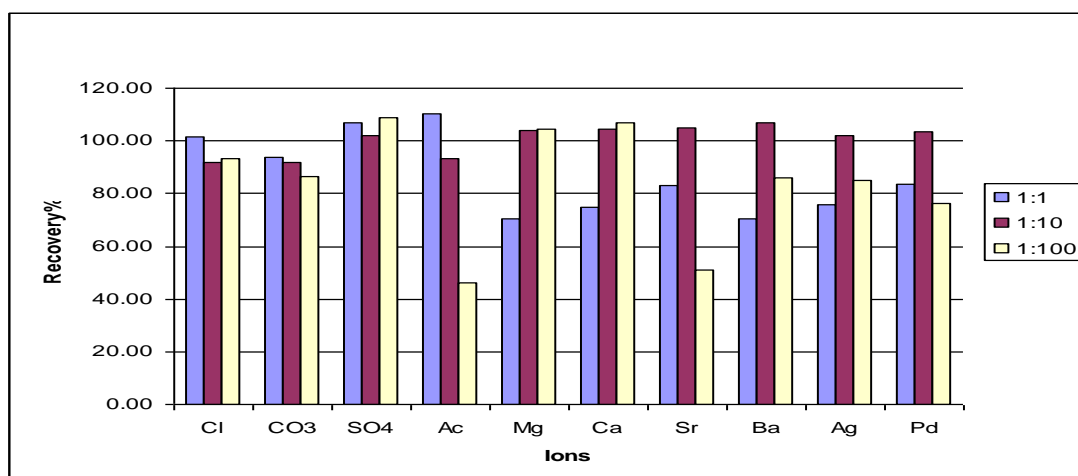


Figure 3: Effect of foreign ions on adsorption of Pb(II) ion on silica gel coated with PS Schiff's base.

The presence of anions such as chloride, sulphate and carbonate did not interfere even at high concentration levels and also some cations such as Mg, Ca, Sr and Ba did not affect the recovery of Pb even in 100- fold related to the Pb concentration. Acetate ion has a significant interference on the recovery at high concentrations (1:100) also strontium in the same level.

3.4. Figure of merit

Under the previously optimized conditions the analytical figures of merit of the developed procedure were determined. The data were analyzed by least squares method and the best straight line was drawn with a correlation coefficient of 0.9986. The limit of detection was 19.5 ng mL⁻¹ obtained by the equation $LOD = KS_b/m$, where $K = 3$, m is the slope of the calibration curve and S_b is the standard deviation of ten replicate readings of the reagent blank performed under the general procedure.

3.5. Real Samples measurements

3.5.1. Accuracy and application

The method was applied to the separation and recovery of Lead ion from water samples spiked with certain amount of Lead ions. 50ml samples of drinking water from the market were taken as synthetic matrix to test the ability of the sorbents to separate Pb ions. The results are shown in table (1).

Tabel 1: Analysis results of water samples.

Pb(II) introduced, μg	Found, μg
0.00	N.D.
25	25.41 ± 1.51
50	50.33 ± 4.43
75	74.70 ± 1.02

N. D. = Not detected

As is seen from the results, good agreement is observed between the introduced and the found amounts of test ion. These results prove the accuracy of the procedure. Also 250 and 500 ml samples of bottled drinking water from the market were spiked by 50 μg Lead. The amount of lead has been determined by the proposed method and the results were $52.30 \pm 1.31 \mu\text{g}$ and $52.75 \pm 0.32 \mu\text{g}$ for 250 and 500 ml samples respectively.

4. Conclusions

The results presented in this work demonstrate the suitability of silica gel coated with Schiff's base as an adsorbent for column pre-concentration of lead. The pre-concentration procedure described in this paper allows lead determination at low level in various water samples, whose analysis would be restricted due to poor sensitivity of flame atomic absorption spectrometry. The selectivity was excellent, making it possible to detect and determine lead in the presence of high concentration of foreign ions. The detection limit achieved was satisfactory for the sample studied. In addition this method is sensitive, low cost, mainly if more sophisticated techniques such as ICP-OES or GF-AAS are not available. In comparison to other solid phases, large pre-concentration factor was achieved. The proposed procedure can be successfully applied for the determination of lead in the different water samples with good recoveries.

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