Spectrophotometric Determination of Lead in Environment Samples by Benzoic Acid Azo PhenylCalix[4]arene (BAPC)

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Abstract

A new and selective spectrophotometric method for the determination of trace amounts of Pb(II) in aqueous environmental samples is reported. The interaction in solution between Pb(II) and Benzoic acid Azo Phenyl Calix[4]arene (BAPC, **1**) was studied. Upon reaction of PABC and Pb(II) a stable complex is formed. Under the conditions reported here the method furnishes reproducible results with basic media. The calixarene derivative shows strong binding ability to Pb^{2+} ion with formation of a 1:1 complex. Beer's law is obeyed in the range of $2.0 \times 10^{-6} - 2.4 \times 10^{-5}$ $molL^{-1}$ of Pb^{2+}. The apparent molar absorptivity (ε) of **1**-Pb^{2+} complex was 1.89×10^4 $Lmol^{-1}cm^{-1}$ at 440 nm, and the detection limit is 1.4×10^{-6} mol L^{-1}. The calixarene **1** showed high sensitivity and selectivity for Pb^{2+}. The method was used to determine the content of Pb(II) in synthetic and natural samples.

Keywords: Spectrometry, Determination of lead traces, Water, Vegetable, Vetiver-grass, Azo-calixarene

1. Introduction

Lead is a cumulative poison that enters the body from lead water pipes, lead-based paints and leaded petrol (Renner, R. 1995). 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 acute lead poisoning can result in colic shock, severe anemia and irreversible brain damage. Lead compounds as antiknocking agents in automobile fuels cause air pollution.

The determination of trace amounts of lead is very important in the context of environmental monitoring. Atomic absorption and atomic emission spectrometry are used for routine trace analysis of lead, however a large number of spectrometric methods for determination of lead are reported to face interference due to the presence of several metal ions (Table 1) (Du, B. et. al 2002, Fargussion, J.1990, Ferreira, S. L. C. et.al 1991, Dutta, S. & Das, A. K. 2007, Kiehei, U. et. al 2000, Mondal, B. C., Das, A. K. 2002, Dutta, S. & Das, A. K. 2007). For this reason there is an ongoing search for new organic reagents for direct and rapid spectrophotometric determination of trace amounts of lead, especially in aqueous solutions.

The structure elucidation of Benzoic acid Azo Phenyl Calix[4]arene (BAPC) was reported in our previous papers (Kim, T. H. et. al 2007, Kim, T. H. et. al 2008). Based on these findings, this paper reports a spectrophotometric method with a new reagent for a simple, fast, and sensitive determination of Pb(II) traces without preconcentration. The formula of the BAPC reagent is shown in Fig. 1.

2. Experimental

2.1 Reagents

All chemicals were analytical reagent grade. Water was purified and distilled. A stock solution of **1** (1.0×10^{-3} mol L^{-1}) was prepared in MeCN. Lead perchlorate stock solution (2.0×10^{-2} mol L^{-1}) was prepared in water. The Pb^{2+} solution was diluted 10 and 100 times to give 2×10^{-3} mol L^{-1} and 2×10^{-4} mol L^{-1} solutions. A working standard solution of Pb^{2+} (2.0×10^{-5} mol L^{-1}) was prepared from this stock solution by dilution with distilled water.

KCl–NaOH buffer solution (pH = 12.5) was used. Aqueous solutions with 0.010 mol.L^{-1} concentrations of different cations were obtained by dissolving the appropriate substance in distilled water.

2.2 Apparatus

Absorption spectra were measured with a Varian-5000 UV-visible spectrophotometer (USA).

2.3 Procedure

The solutions to be studied were prepared in 10 mL volumetric flasks. Measured volumes of Pb(II) and organic reagent solutions were introduced in the flasks and they were filled up to the mark with KCl-NaOH buffer solution (pH = 12.5). Absorbance of each solution was measured against a corresponding blank reagent similarly prepared.

2.4 Collection of water, Vetiver grass and soil samples

Soil, water and vetiver grass samples were collected from points in Kontum province (Vietnam). Vetiver grass (scientific name *Vetiveria zizanioides L.*), a robust and easily propagating species capable of adapting to a wide range of climate and soil conditions, requires little care. Vetiver grass grows as bushes. The slabs are relatively hard and most leaves are at the base. With its dense roots Vetiver grass is able to absorb toxic minerals such as N, P, Al, Mg, Hg, Cd and Pb (Troung, P.N.V., Baker, D. 1998) from fertilizers and pesticides thus preventing pollution of soil and water. In addition, Vetiver grass also helps to increase the soil fertility by means of a natural moisturizing effect. The grass roots and its dense body will retain soil and mud on the surface. Stems, leaves and grass roots when buried in soil will break down to organic material, make the ground more soft and airy, thus improving the mechanical properties of soil (Ilker, A., & Metin, T. & Quirine, M. K. & Avni, C. 2008).

Vetiver grass samples were collected carefully using a hand shovel to dig out the soil around the grass. The plants were pulled out carefully, ensuring that no part of the root was lost. The different grass samples were kept individually in properly labelled polyethylene bags. Soil samples were collected from the same point where the grass samples were uprooted. The soil samples were collected to a depth of 15 cm using a soil auger. The soil samples were kept in labelled polyethylene bags. One litter of water was collected for lead determination in water. Polypropylene bottles used for the water samples were previously rinsed with deionized water and 30% HNO_3. The samples were brought to the laboratory and kept in the fridge prior to analysis for lead.

2.5 Sample preparation

Each grass sample was separated into leaves, roots, and stems and dried in an oven at 50 ºC for 8 hours. The dried plant samples were milled using a laboratory blender and kept for digestion. Unwanted materials such as stones, leaves and debris were removed from the soil samples by handpicking. The soil sample was further broken down into finer particles using a laboratory mortar and pestle. The soil samples were dried in an oven for 8 hours at 80 ºC (Douglas, C. B., Wolfgang, F. 1995).

2.6 Sample digestion

Plant sample digestion

Grass samples were digested following the method of Allen et al. 3g of the milled plant sample were weighed into a conical flask using a digital weighing balance. 3 ml of 60% hydrochloric acid and 10 ml of 70% nitric acid were added to the weighed milled plant sample. The conical flask was then placed on a laboratory hot plate for digestion until the white fume evolving from the conical flask turned brown. The mixture was allowed to cool and then filtered through a Whitman's filter paper, leaving a whitish residue. The filtrate was then filled up to 25 ml with distilled water and stored for analysis.

Soil sample digestion

The same procedure for the digestion of plant sample was used according to the method of Allen et al.

3. Results and Discussion

3.1 Absorbance spectra

The spectrum recorded for a solution containing Pb(II) and organic reagent are presented in Fig.2(a). A chemical interaction between Pb(II) and organic reagent has occurred. The maximum absorption of the complex is located at 440 nm.

3.2 Influence of the pH

The effect of pH on the absorption efficiency is shown in Fig.2 (b), which indicates that high deposition efficiency was achieved at pH 12-13. The maximum and constant absorbance of the complex is obtained in the pH range of 12.3–12.7, and a pH of 12.5 may thus be chosen for the following experiments. At pH = 12.5, the effects of four

kinds of buffers on the absorbance were also examined. KCl–NaOH buffer solution was chosen.

3.3 Stoichiometry of the complex

The effect of reagent concentration was examined by measuring the absorbance of the solution containing a known concentration of Pb(II) and different amounts of organic reagent. The spectrophotometric titration using a constant amount of organic reagent and variable concentration of Pb(II) as well as Job's method were also employed in order to establish the stoichiometry of the complex. The results indicate formation of a complex Pb(II) : PABC = 1 : 1.

3.4 The stability constant

The apparent stability constant of the complex was calculated from the data obtained using the mole ratio method. The value of the stability constant is: 6.2×10^4 mol^{-1} L for PBC. The value of stability constant obtained at $25 \pm 2°C$ show a very stable complex for the corresponding stoichiometry. The absorbance of $\mathbf{1}$-Pb^{2+} complex can reach maximum in 10 min and remain unchanged for at least 3 h.

3.5 Calibration curve

Beer Lambert law is followed for Pb(II) concentration in the $2.0 \times 10^{-6} – 2.4 \times 10^{-5}$ mol L^{-1} (r = 0.9997) of Pb^{2+}. Absorbance $(A) = 0.025 \times C$ (10^{-6} mol L^{-1} of Pb^{2+}) + 0.021 (n = 8, r = 0.99). The molar absorptivity coefficient (ε) is 1.89×10^4 L mol^{-1} cm^{-1}.

3.6 Interferences

The influence of other metal ions such as alkali, alkaline earth, or transition metal ions on the absorption was studied repeatedly with very high concentrations. Results showed that metal ions do not affect the spectrum of the complex. Cu(II), Ca(II), Fe(II), Cr(III), Co(II), Ni(II) have been found to interfere only if their concentration exceeds the lead concentration by a factor or 280-500.

3.7 Determination of Pb(II) in natural samples

The spectrophotometric method was applied to the determination of Pb(II) in water, soil and vertiver grass in Kontum province, VietNam. The comparison of results presented in Table 2 shows good agreements between the values determined by the proposed method and other methods.

4. Conclusion

The calixarene derivative BAPC forms a 1:1 complex with Pb^{2+} suitable for spectrophotometric determination of lead traces in aqueous solution. The optimum conditions for complex formation have been elucidated. The new reagent has been used to analyze samples of water, soil and Vetiver grass in Kontum province. The results showed that this method offers sensitivity comparable to that of the traditional reagents. Advantages of the proposed method are simplicity, rapidity and sensitivity without interference from other metal ions and without sample preconcentration.

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Table 1. Comparision of Analytical Parameters for the Spectrophotometric Determination of Lead

Reagent	λ (nm)	ε_λ x10^{-4} (L.mol^{-1}cm^{-1})	Remark
1-(2-Thiazoylazo)-2-naphthol	575	3,6	Light-sensitive, Co, Zn, Fe, Mn EDTA interfere
Porphyrin compounds	479	2,2	Cu, Ni, Mn, Cd, Ca, Mg, Zn Fe interfere
Diphenylthiocarbazone	520	2,5	Light-sensitive
Phenylazoformic acid 2- phenylhydrazide	525	7,2	
Xylenol orange	580	2,3	Light-sensitive, Hg Zn, Al, Bi, Ni, Re interfere
2-(2-Thiazoylazo)-p-cresol	650	2,1	Ni, Co, Zn, Fe, Cd, Cu interfere
4-(2-Pyridylazo)- resorcinol	520	4,3	Cd, Ni, Cu, Co, Ag, Hg, Zn, Fe interfere
Arsenazo-TB	620	1,8	Light-sensitive, Ti, Th seriously interfere
Diethyl dithiocarbamat acid, Diethylammonium salt	435	1,3	Cu, Hg, Zn, Fe interfere
Arsenazo.III	660	3,0	Al, Cu, Th Ti, U Fe interfere
1 (This work)	440	1.2	Cu, Ca, Fe, Cr, Co, Ni interfere

Table 2. Determination of Lead in environment samples (mg/kg) n=5

Samples	Found by proposed method (mg/kg)	Found by other method (mg/kg)
W35	2.32 ±0.09	2.21 - EPA-method 200.7
W39	1.85 ±0.04	1.98 - EPA-method 200.7
W41	2.12 ±0.10	2.03 - EPA-method 200.7
W42	1.89 ±0.05	2.04 - EPA-method 200.7
W52	4.03 ±0.08	3.90 - EPA-method 200.7
S2	-	- - AAS-Tome II
S160	2.14 ±0.12	2.08 - AAS-Tome II
S68	2.52 ±0.08	2.40 - AAS-Tome II
S10	1.32 ±0.10	1.22 - AAS-Tome II
VG 21	0.75 ± 0.07	0.68 - AOAC 985.01
VG36	1.25 ± 0.06	1.12 - AOAC 985.01
VG47	1.18 ± 0.07	1.15 - AOAC 985.01
VG53	0.98 ± 0.05	0.94 - AOAC 985.01

* W: water, VG: Vetiver grass, S: soil, Number is place
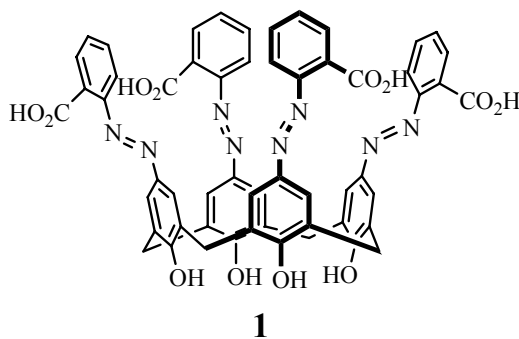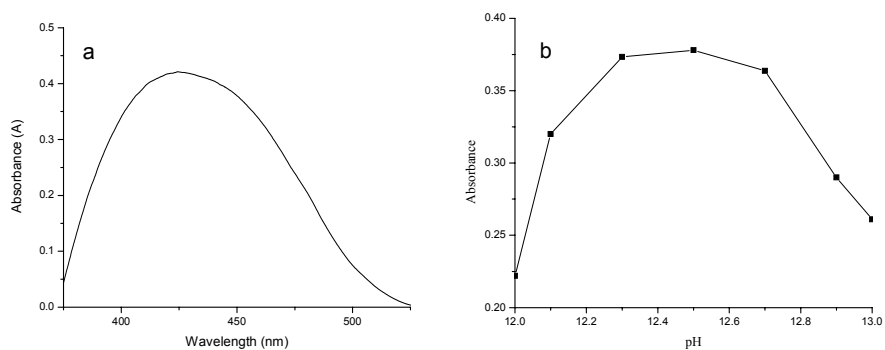

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Figure 1. Structure of Benzoic acid Azo Phenyl Calix[4]arene (BAPC)

Figure 2. Absorption spectra of **2** and its Pb^{2+} complex at pH 12.5 (a) Effect of pH (b)