

Novel Procedure for Detection of Some Heavy Metal Ions in Shrimp Pond by Liquid Phase Extraction with Sodium Acetate

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ABSTRACT

A pre-concentration procedure for liquid phase extraction with sodium acetate and cyclic voltammetric determinations of some heavy metal ions in shrimp pond is presented in this work. In order to achieve accurate, sensitive and reliable results, pre-concentration and separation are needed when the concentrations of analyte metal ions in the primitive material or the prepared solutions are too low to be investigated. The effectiveness of analytical parameters such as pH of the sample solution, flow rate of sample and eluent solutions, sample volumes, on the recoveries of copper and lead were determined. The influences of co-ions were also examined. The presented pre-concentration procedure was used for the determination of metal ions in reference standard material and real environmental samples in sediment.

Keywords: Pre-concentration, liquid phase extraction, sodium acetate, cyclic voltammetry, lead, copper

INTRODUCTION

There is a long history of a relation between humans and metals. Metals are mixed in soil, water and air as impurities, and can be transferred to the body by eating, respiration and volatilization through the skin. Some metals are essential elements for animals and plants. On the other hand, excess metal ions can be toxic and hazardous to human cells.

In recent years, contamination of the environment by heavy metals has become a major source of pollution. For example, copper is an essential element for metabolic processes, to build hemoglobin and synthesize enzymes. However, excess copper can be toxic and harmful to human cells, causing pain, bleeding in the stomach, and ultimately diarrhea. Additionally, it can cause a rash on the skin and irritate the eyes. In contrast, lead is not an essential element for animals and plants, but is still highly toxic leading to stomach problems and an inability to biosynthesize hemoglobin and other enzymes [1].

The heavy metal concentration can be determined not only in soil, sediment, water, and air but also in aquatic animals such as fish and shrimp. The exports of shrimp farms generate large amounts of foreign exchange into Thailand. Indeed, the shrimp exports earned Thailand annually more than twenty billion baht last year. However, the shrimp farm industry has problems from epidemics, chemicals, biological products including heavy metal contaminants in waste water from domestic and industrial use. In general, heavy metals collect in mangrove areas more than gulf coast areas. Shrimp farms are often in mangrove areas because they provide an ideal environment for shrimp growth. In nature, shrimp eat food which is covered with surface sediment, a cause of heavy metal contamination in the shrimp.

Cyclic voltammetry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. This paper reports its use in a very sensitive, highly specific voltammetric method for the trace determination of lead and copper. The pre-concentration procedure is more sensitive than other methods, with respect to accuracy, sensitivity, selectivity, simplicity, speed, pH range, precision, and ease of operation. The procedure is based on extraction with sodium acetate of the sediment samples. The particular resin is used to increase detected signals.

The aim of this study was the determination of lead and copper in sediments to provide information for shrimp farmers to encourage them to be more cautious and reform the safety standards in shrimp farming in relation to heavy metal contaminants.

MATERIALS AND METHODS

Apparatus

A voltammeter (Metrohm Model-PGSTAT 100) and 633VA stand equipped with Pt-rod, Ag/AgCl, and glassy carbon electrodes and a pH meter (Orion Model-420A) with combination electrodes were used for measurements of absorbance and pH, respectively. An atomic absorption spectrometer (Perkin-Elmer Model-Analyte 300) equipped with a microcomputer-controlled acetylene flame was used for comparison of the results.

An appropriate amount of resin was suspended in D.I. and cleaned with 0.5 M HNO₃ until a clear aliquot was obtained. The column was packed with Dowex 1×8 chloride form resin and then cleaned with 1.2 M Hydrochloric acid - 10 % Sodium chloride. The resin was used repeatedly after washing with 1.2 M Hydrochloric acid - 10 % Sodium chloride.

Reagents and Solutions

All chemicals used were of analytical-reagent grade. Doubly distilled de-ionized water was used. The standard and samples were acidified with HNO₃. The eluents were prepared by dissolving the appropriate amount of solid reagent (Merck) in deionized water.

Glass and plastic vessels were cleaned by soaking in 20 % HNO₃ overnight and rinsed several times with high-purity de-ionized water. The sediments were stored in acid-washed polypropylene bottles containing dry air.

A certified stock standard Pb(II) and Cu(II) solutions (1000 ppm) in HNO₃ were obtained from Merck. The working standard solutions were daily prepared by the appropriate dilution with HNO₃ from a 1000 mg l⁻¹ atomic absorption standard solution (Merck).

Sample collection

The sediments were collected from 4 shrimp ponds, obtained on the campus of Walailak University, Thasala, Nakhon Si Thammarat, Thailand. They were collected at approximately 30 cm depth from the water surface. All samples were stored in a plastic bag prior to analysis. They were used to determine the concentrations of copper and lead.

Sediment Preparation

The sediment was prepared by heating in an oven, followed by grinding, and were packed in plastic bags. The samples were preserved in dry air, to complete dryness.

Digestion of Sediment Solution

Approximately 0.4 g of sediment was digested in a mixture of concentrated hydrochloric and nitric acid by a microwave digester. The instrument parameters used were those recommended by the manufacturer. At the completion of the microwave digestion, the colorless samples were transferred to 100 ml volumetric flasks and made up to volume with deionized water, and stored in polypropylene bottles.

Pre-concentration Procedure

The solutions were set into three following procedures:

1. The eluate was pipetted into a conical flask and 1 M sodium acetate was added. The solution was then left for 1 h. Later, some heavy metals were determined by voltammetry and flame atomic absorption spectrometry.

2. The eluate was pipetted into a conical flask and 0.04 M hydroxylamine hydrochloride was added. The final mixture was left for 6 h at 96 °C. Later, some heavy metals were determined by voltammetry and flame atomic absorption spectrometry [2].

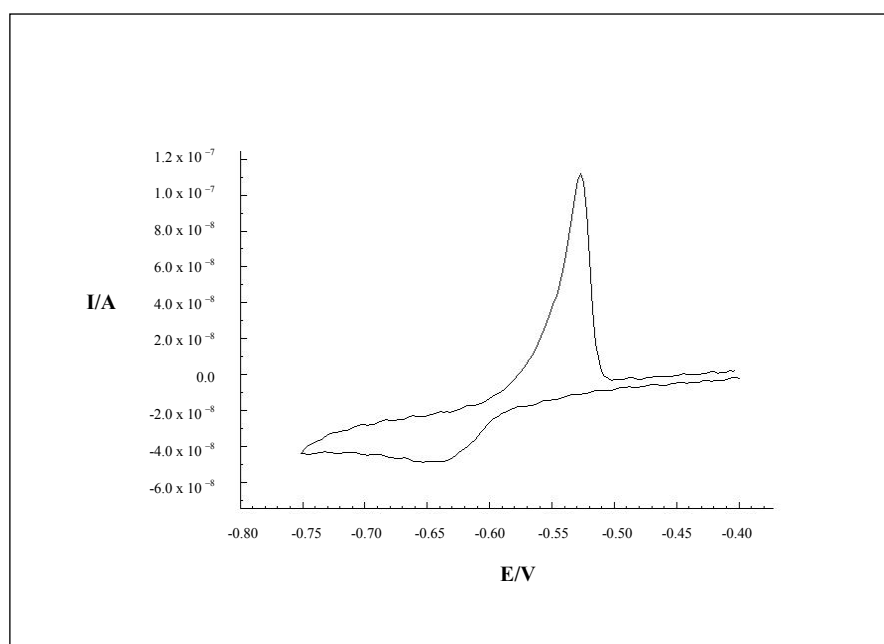
3. The eluate was pipetted into a conical flask and 0.02 M nitric acid and 30 % hydrogenperoxide were added. The final mixture was left for 2 h at 85 °C. Later, some heavy metals were determined by voltammetry and flame atomic absorption spectrometry.

The three pre-concentration procedures were used and the results from each procedure compared to determine the best pre-concentration procedure.

RESULTS AND DISCUSSION

Voltammograms

The voltammograms of lead and copper in sodium acetate were recorded using a voltammeter (**Figure 1**). The voltammogram of lead reveals a peak with the maximum at -0.53 V. while that of copper is observed at -0.12 V.



(a)

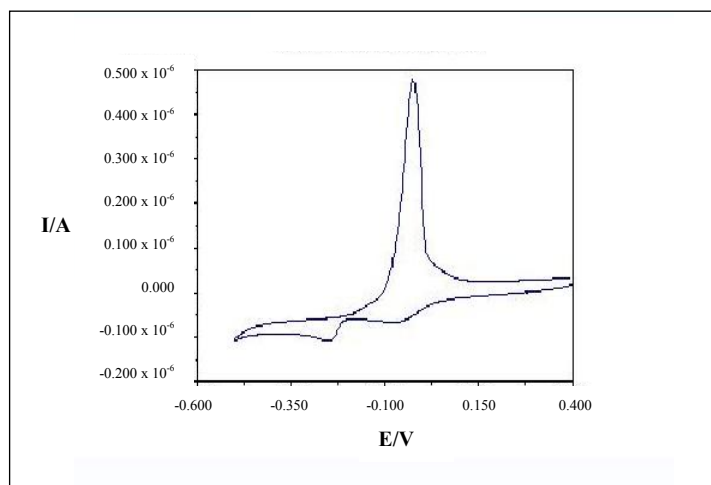
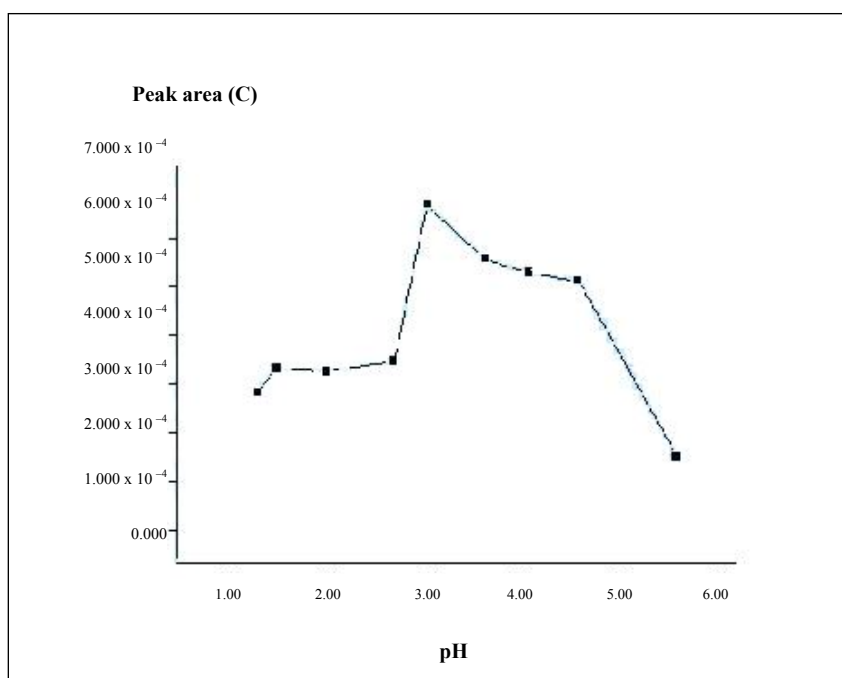


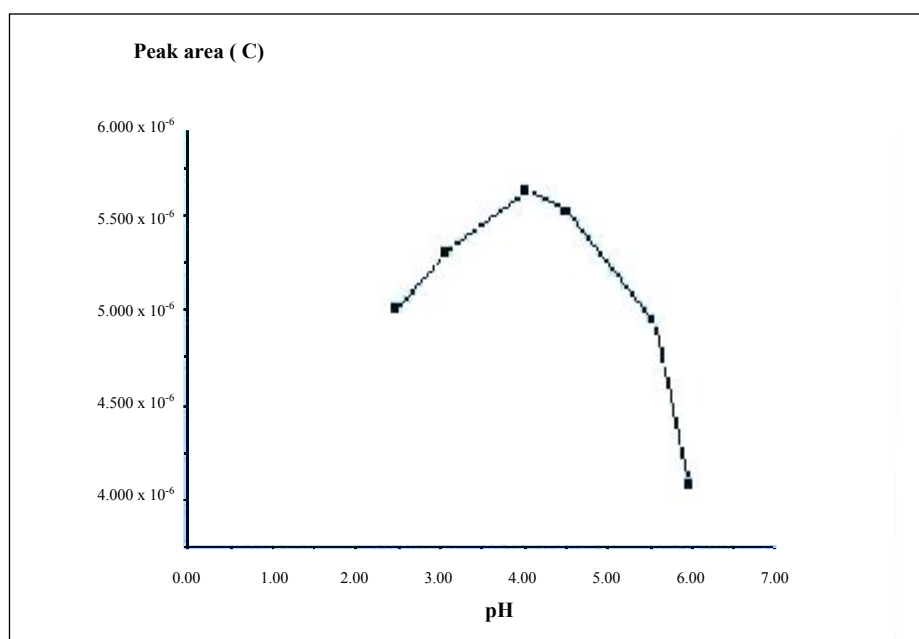
Figure 1 Voltammograms of the determination of (a) lead and (b) copper.

Effect of acidity

Acetic acid was found to be the best acid for the system. The effect of pH on the peak current (**Figure 2**), shows that the sensitivity increases when the pH is between 1 and 7, whereas at higher pH values sensitivity decreases. Very high pH values were not tested because of the possibility of the hydrolysis of lead and copper ions in the solution. pH values of 3.0 and 3.5 were selected for further optimization as they are optimal for the study of lead and copper in sediment.



(a)

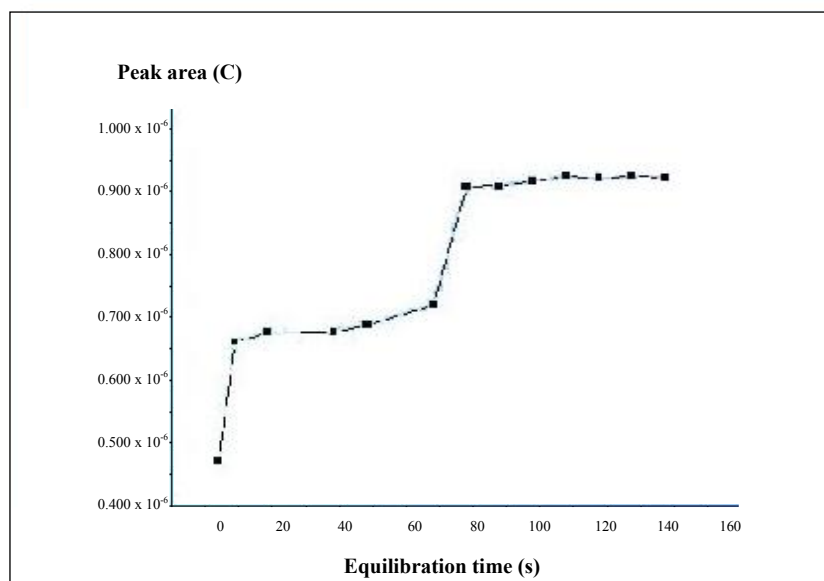


(b)

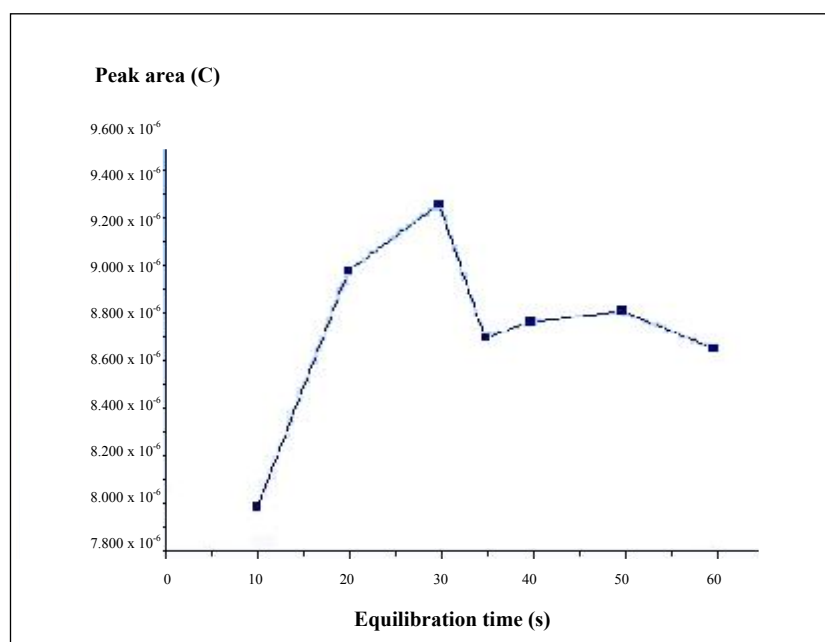
Figure 2 Effect of varying voltammetric parameters: peak area versus variation of the pH in the sediments for (a) lead and (b) copper.

Effect of Deposition Time

When the reaction was stable, deposition times between 5 and 180 s were studied. Constant maximum potential was obtained around 115 and 30 s for the determination of lead and copper, respectively. The effect of deposition time on the peak current is shown in **Figure 3**.



(a)

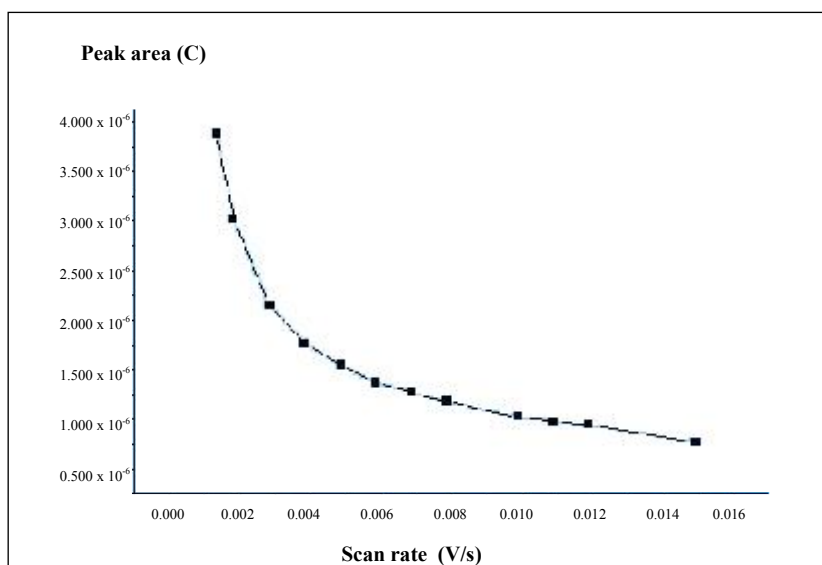


(b)

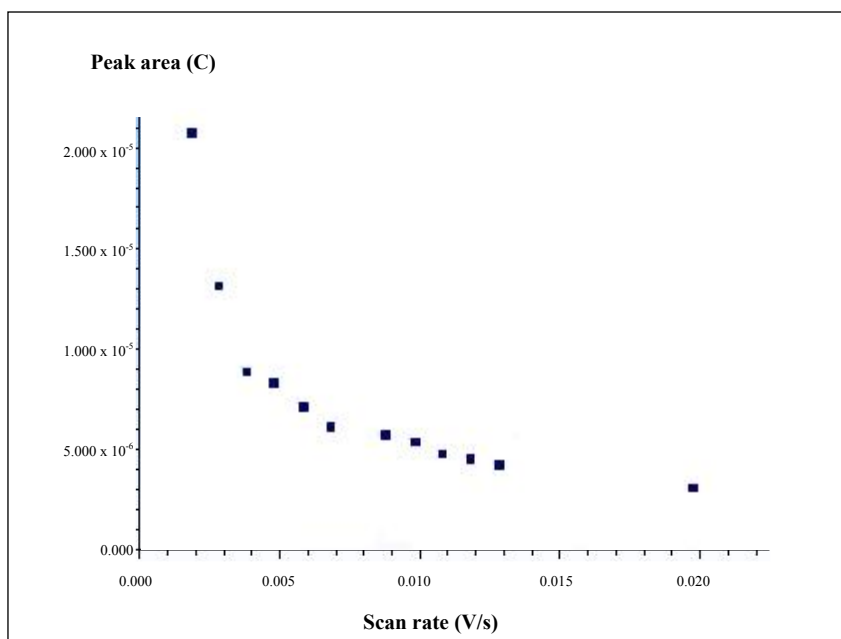
Figure 3 Effect of varying voltammetric parameters: peak area versus variation of the deposition time in the sediments for (a) lead and (b) copper.

Effect of Scan Rate

The effect of scan rate on the peak area for lead and copper are shown in **Figure 4**. The potential was varied between +0.001 and +0.015 V/s. The peak area was found to decrease with increasing deposition potential up to +0.015 V/s. An optimum scan rate of +0.008 V/s and +0.005 V/s were selected for further study for lead and copper, respectively.



(a)

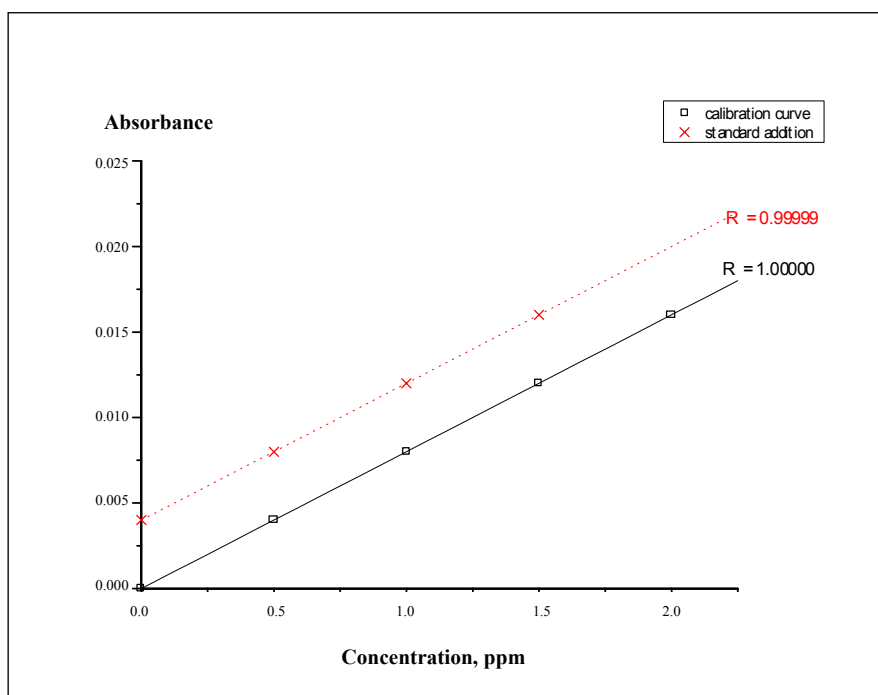


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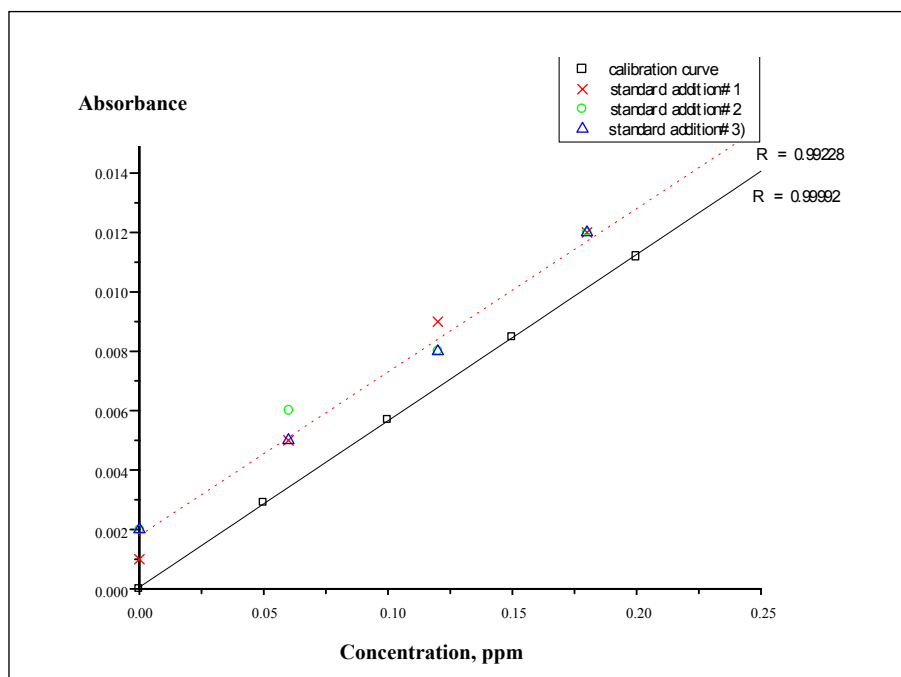
Figure 4 Effect of varying voltammetric parameters: peak area versus variation of the scan rate in the sediments for (a) lead and (b) copper.

Calibration and Standard Addition Curves

The complex stability of lead and copper with EDTA was determined after pre-concentration. Therefore, EDTA additions were made to sediment solutions in a ratio 1:1 weight by weight. The metals tend to be fully complexed in buffer solutions. The recovery of lead and copper was 115 and 98 % respectively.



(a)



(b)

Figure 5 Calibration and standard addition curves in the post-concentration sediment solution for (a) lead and (b) copper.

The calibration and standard addition curves of lead and copper are shown in **Figure 5**. Both calibration and standard curves were in parallel suggesting that there was no matrix interference. In order to prove this supposition several sample solutions were added with co-ions, such as copper, lead, cadmium, and zinc [3]. No effect was noted in these analyses. The detection limits for this procedure are 9.94×10^{-3} mg/l for lead and 5.37×10^{-2} mg/l for copper.

Determination of Lead and Copper in Sediments

Aliquots of post-concentrated sediment sample were analyzed. The quantities of lead by flame atomic absorption spectrometry (FAAS) and cyclic voltammetry (CV) are shown in **Table 1**.

Table 1 Lead concentration in digested sediment solutions. Note: % difference refers to the lead concentration as detected by CV and FAAS.

Samples	Concentration (ppm)		% differences
	By CV	By FAAS	
SED 1	0.312	0.289	- 7.95
SED 2	0.187	0.196	+ 4.59
SED 3	0.228	0.222	- 2.70
SED 4	0.238	0.248	+ 4.03

It showed that the lead content in digested sediment solutions detected by cyclic voltammetry (CV) were in the range of 0.187 to 0.312 ppm. The results agree well with those obtained by FAAS.

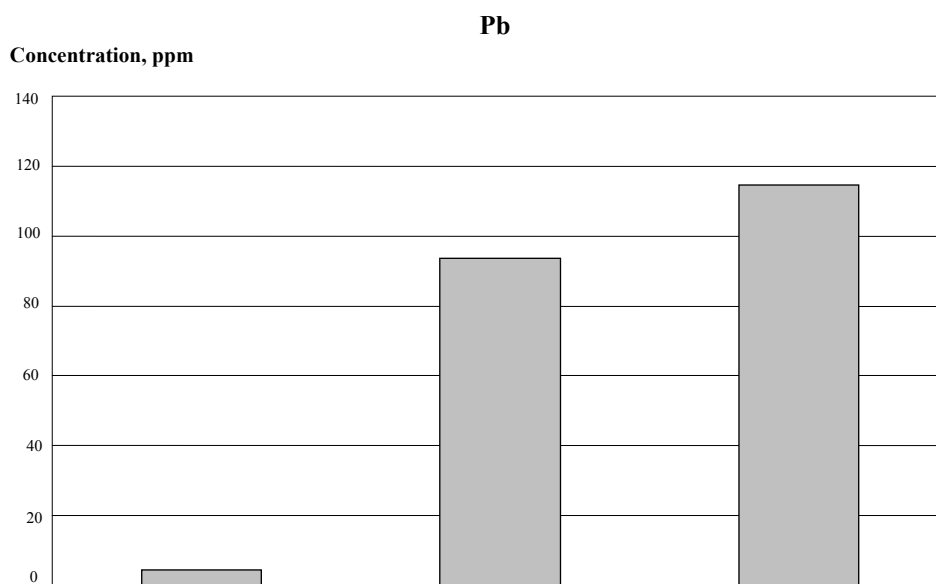
METHOD DEVELOPMENT

The goal of this work was the development of a method for the determination of lead and copper in environmental samples at concentrations below the detection limit of conventional FAAS. The strategy adopted here was to consider how to increase the sensitivity, then evaluate the effect on the detection limit obtainable, and finally measure the accuracy by the analysis of spiked samples against aqueous standards. Dowex 1×8 chloride form resin was used as the solid phase while sodium acetate was used as a liquid phase for extraction [4,5].

The concentration of lead and copper after the pre-concentration procedure 1 - 3 is shown in **Table 2** and comparison of the results in **Figure 6**. The concentration of lead was considerably higher 500, 400 and 400 times respectively, and 200, 160 and 160 times respectively for copper (**Table 2**). From **Table 2** the pre-concentration procedure 1 gave the highest concentrations of lead and copper. In all cases these results indicate that the pre-concentration procedure may be successfully applied to the separation and determination of trace lead and copper in real environmental samples.

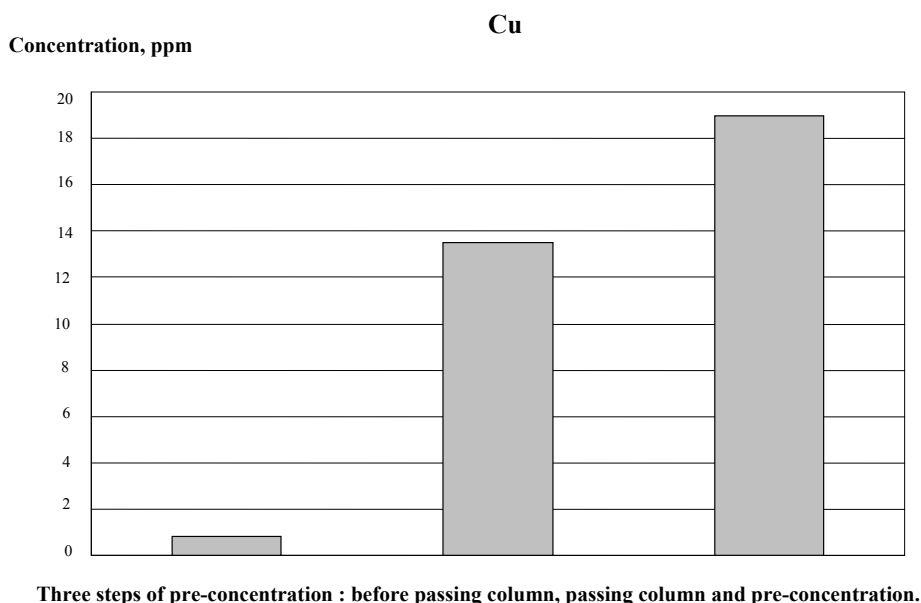
Table 2 The concentration of lead and copper in digested sediment solutions by various pre-concentration procedures by FAAS, ppm.

	Concentration (ppm)	
	Pb	Cu
Before passing column	0.174	0.080
After passing column	3.750	1.350
Pre-concentrate procedure 1	114.500	19.000
Pre-concentrate procedure 2	82.000	13.500
Pre-concentrate procedure 3	79.500	14.500



Three steps of pre-concentration : before passing column, passing column and pre-concentration.

(a)



(b)

Figure 6 Comparison of (a) lead and (b) copper concentrations in digested sediment solutions at three steps of pre-concentration: before passing column, passing column and pre-concentration.

The concentration of lead and copper was considerably higher than those in digested sediment solutions approximately 500 and 200 fold respectively. The precision for analysis of lead and copper in sediment samples (n = 9), expressed as relative percentage standard deviations was 11.51 and 9.5 % respectively (**Table 3**).

Table 3 The precision of the concentration of lead and copper in digested sediment solutions, ppm as determined by FAAS.

Sample No.	Pb			Cu		
	Mean	SD	% SD	Mean	SD	% SD
SED1	78.861	12.996	16.48	8.139	0.772	9.48
SED2	76.083	8.792	11.55	9.361	0.532	5.68
SED3	80.594	7.974	9.89	11.111	0.928	8.35
SED4	87.306	9.632	11.03	11.833	0.952	8.04
SED5	96.528	8.326	8.62	13.083	0.901	6.89

The concentration of lead and copper in sediments was determined using cyclic voltammetry. The optimum conditions involve using a glassy carbon working electrode, a Ag/AgCl reference electrode and a Pt rod auxiliary electrode at scan rates of 8 mV/s for lead and 5 mV/s for copper. The optimum equilibration times were found to be 115 s and 30 s for lead and copper respectively and the pH of the solutions were 3.0 and 3.5 respectively. The contents of lead and copper in the digested sediment solution were in the range of 0.02 to 0.06 ppm and 0.19 to 0.31 ppm respectively (**Table 4**). The detection limit for this procedure was 9.94×10^{-3} mg/l for lead and 5.37×10^{-2} mg/l for copper.

Table 4 The concentration of lead and copper (ppm) in digested sediment solutions, ppm as determined by cyclic voltammetry.

Sample No.	Pb		Cu	
	CV	FAAS	CV	FAAS
SED1	0.06	0.05	0.31	0.29
SED2	0.04	0.04	0.19	0.20
SED3	0.03	0.04	0.23	0.22
SED4	0.02	0.02	0.24	0.25

CONCLUSIONS

Employing this procedure, the concentration of lead and copper in digested sediment solutions was determined using cyclic voltammetry. The optimum conditions involve using a glassy carbon working electrode, a Ag/AgCl reference electrode and a Pt rod auxiliary electrode at scan rates of 8 mV/s, an equilibration time of 115 s and a solution pH of 3.0 for lead. The lead concentration is in the range of 0.02 to 0.06 ppm. For copper, a scan rate of 5 mV/s, an equilibration time of 30 s and a solution pH of 3.5 are used. The copper concentration is in the range of 0.19 to 0.31 ppm. The detection limits for this procedure are 9.94×10^{-3} mg/l for lead and 5.37×10^{-2} mg/l for copper. The results agree well by comparison with those obtained by Flame Atomic Absorption Spectroscopy ($t = 1.814$, $P = 0.05$, $n = 4$) (**Table 1**).

In this paper, a novel, simple, selective, sensitive procedure was developed for the determination of lead and copper in soil samples, for continuous monitoring of trace levels of lead and copper in complicated sample matrices. Spectrophotometry remains a popular technique due to the

low cost of the instrument, ease of operation, and almost no maintenance cost. Voltammetry is an alternative technique to determine the concentrations of lead and copper in environmental samples. The sensitivity in terms of area and precision of the present method is very reliable for trace analysis down to ng g^{-1} levels in aqueous solution at room temperature.

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บทคัดย่อ

สราวุธ เดชมนี และ อัจฉรวรตี ชูย์มพานิช

วิธีการวิเคราะห์โลหะหนักบางชนิดในตะกอนบ่อกึ่งโดยวิธีการสกัดแบบของเหลวด้วยโซเดียมอะซิเตท

งานนี้เป็นการเสนอวิธีการเตรียมอออนสำหรับการสกัดในสถานะของเหลวด้วยโซเดียมอะซิเตทและการวิเคราะห์หาอออนของโลหะหนักบางตัวโดยวิธีไซคลิกโวลแทมเมทรี เพื่อต้องการความแม่นยำความไวและผลที่น่าเชื่อถือ จึงต้องมีการเตรียมและการแยกสารในขณะที่ความเข้มข้นของสารที่ต้องการวิเคราะห์ในวัตถุบหรือในสารละลายที่เตรียมขึ้นมีความเข้มข้นในระดับต่ำ ตัวแปรที่จำเป็นต้องคำนึงถึง ได้แก่ ค่าพีเอช อัตราการไหลของสารตัวอย่าง และสารละลายที่ใช้เป็นตัวชะ ปริมาตรของสารตัวอย่าง เป็นต้น ขณะหาค่าการกลับคืนของโลหะทองแดงและตะกั่ว อิทธิพลของอออนที่อยู่ร่วมกันก็ถูกวิเคราะห์ วิธีการเตรียมสารนี้ได้ใช้ในการวิเคราะห์หาอออนของโลหะจากสารตัวอย่างมาตรฐานและตัวอย่างจริงในสิ่งแวดล้อมที่เป็นตะกอนดิน