

## **The Study and Invention of Portable Voltammetry for Detecting Contamination Heavy metal**

Ph. Thipnet<sup>1</sup>, P. Sawangwong<sup>2</sup> and Ch. Issro<sup>3</sup>

<sup>1</sup>*Environmental Science Program, Faculty of Science, Burapha University, Chon buri, Thailand*

<sup>2</sup>*Environmental Science Program, Faculty of Science, Burapha University, Chon buri, Thailand*

<sup>3</sup>*Department of Physics, Faculty of Science, Burapha University, Chon buri, Thailand*

---

**Abstract:** *In this work, an alternative voltammetric procedure for the simultaneous determination of lead(Pb), cadmium(Cd) and copper (Cu) were developed by using microcontroller for inventing portable voltammetry. The electrode that used gold wire, platinum wire and silver wire for working electrode, reference electrode and counter electrode respectively. The electrode can be easily prepared and showed a good analytical response was linear in the range of  $0.5 \mu\text{g L}^{-1}$  to  $50 \mu\text{g L}^{-1}$ . The detection limits of  $0.09 \mu\text{g L}^{-1}$  for Pb,  $0.15 \mu\text{g L}^{-1}$  for Cd and  $0.13 \mu\text{g L}^{-1}$  for Cu. The high sensitivity and good reproducibility of the nontoxic gold wire, platinum and silver wire electrode make it possible to apply the electrode to a portable system for a trace metal analysis. In conclusion, the portable heavy metal meter is easily taken, used and low cost.*

**Keywords:** *Heavy metal, electrochemical techniques, Voltammetry, Microcontroller, Tap water*

---

### **I. Introduction**

Lead Cadmium and Copper are serious environmental pollutants, which are highly toxic to human nervous, immune, reproductive, and gastrointestinal systems. Moreover, these heavy metals are inclined to persistently retain in the ecosystem and bio-accumulate in human body through food chain. Nevertheless, heavy metals have been extensively exploited and discharged in various manufacturing, mining and casting industry, causing a wide dispersion in the environment. Among all approaches that are capable of trace heavy metal detection, Inductively coupled plasma-optical emission spectrophotometer (ICP-OES) [1], Atomic absorption spectroscopy (AAS) [2], Graphite furnace atomic absorption spectrometry (GFAAS) [3], and inductively coupled plasma mass spectrometry (ICP-MS) [4] are the commonly used methodologies. However, that methodologies always require expensive instrumentation, complicated operation procedures, long detection period and skill personnel.

Electrochemical analysis is a powerful analytical technique that is utility in Pharmaceutical industry, metal industry, and environmental applications. Electro analysis of high advantages due to high sensitivity, reduction in solvent and sample consumption, high-speed analysis, low operating cost and high scan rate in all cases. Several electrochemical techniques, such as voltammetry. Carbon electrodes have been widely used for voltammetric analysis. These techniques were well established for the low cost production, reproducibility, and ease the miniaturization. Numerous advantages diversified chemicals of food quality, clinical and environmental interest and sensitive electrochemical sensors, Screen-printed sensors have been widely used for environmental, biomedical and industrial monitoring.

Electrochemical methods, especially electrochemical stripping analysis, have been widely recognized as a powerful tool for determination of heavy metals due to its low cost, easy operation, high sensitivity and selectivity. Traditionally, mercury electrodes are employed for stripping analysis. However, the toxicity of mercury makes it undesirable for sensing application, particularly those involving food contacts. A great variety of electrode materials has been proposed as alternative such as gold, platinum, carbon, etc.

In this present study, the portable heavy metal meter for detecting contamination in Tap water and Water Sample

### **II. Materials and Methods**

#### **2.1 Reagent and solution**

All chemicals used in the preparation of stock solution were of analytical reagent grade and obtained from Merck Germany and Fluka. Concentrated  $\text{CH}_3\text{COOH}$  p.a. and  $\text{CH}_3\text{COONa}$  solutions were used for the preparation of 1M stock acetate buffer (pH5.5).  $1000 \text{ mg L}^{-1}$  standard solution of Pb, Cd and Cu (spectroscopic grade) (Merck, Germany). Concentration in the stock solution for standard curve were compare from graphite furnace atomic absorption spectrometer (GFAAS). In the preparation of solution, tap water sample were collect in 100 ml from the local area of Chon buri province, Thailand in the month of February 2016 for the determination of Pb Cd Cu and analyzed in same day.

## 2.2 Preparation the electrode

A three-electrode was employed for Portable Heavy Metal Meter for detecting (voltammetry). A gold wire was used as the working electrode. A platinum wire and a silver wire were used as the counter electrode and reference electrode

**2.2.1** Platinum wire cleaning, Rinse platinum with deionized water thoroughly and immerse it in 10% HNO<sub>3</sub> at room temperature to oxidize contaminant from Platinum wire surface. After 10 minutes was reached, rinse it with deionized water thoroughly and let dry in air.

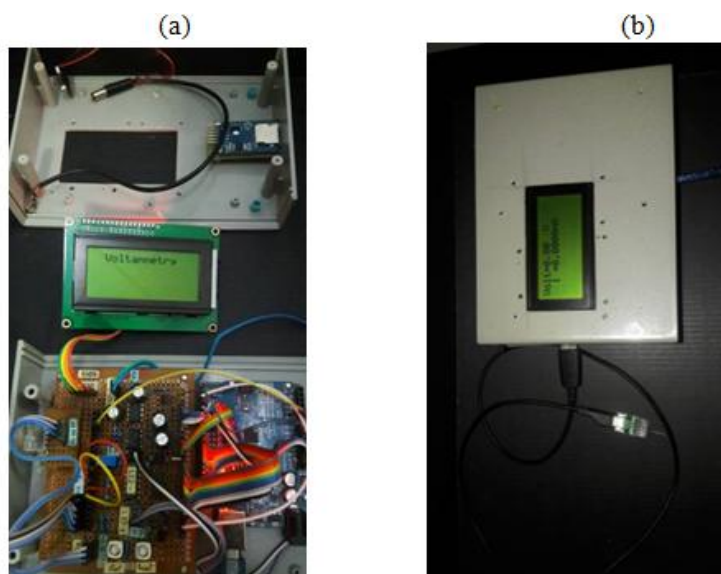
**2.2.2** Gold wire cleaning, Rinse gold with deionized water thoroughly, Immerse it in 10% HNO<sub>3</sub> at room temperature to oxidize contaminant from gold wire surface. After 10 minutes was reached, rinse it with deionized water thoroughly and let dry in air.

**2.2.3** Silver wire cleaning, Rinse silver with deionized water thoroughly, and immerse it in 10% HNO<sub>3</sub> at room temperature to oxidize contaminant from silver wire surface. After 10 minutes was reached, rinse it with deionized water thoroughly and let dry in air.

## 2.3 Invent auto variable power supply and voltmeter ammeter keep data to micro SD

Experiment step for Invent meter, voltmeter ammeter and power supply (mini voltammetry tool)

- 1 Make variable power supply circuit 0-5V by Arduino IDE (microcontroller).
- 2 Add A to D 16 bit module (ADS1115 module)
- 3 Make negative power supply circuit -5V by IC ICL7660
- 4 Make inverting OP-AMP for variable negative power supply
- 5 Make program control power supply -1.7V to 1.7V by Arduino IDE.
- 6 Make program memory value to SD card.
- 7 Display value to LCD display. (Fig.1)



**Fig.1** Portable voltammetry for detecting contamination heavy metal (a) show PCB (b) show USB to electrode

The step for the program on portable heavy metal meter (Portable voltammetry) (Fig. 2)

- 1) Connect USB electrode dip electrode in sample.
- 2) Start program to push button switch "start"
- 3) Voltammetry portable will scan start voltage -1.7v to 1.7v
- 4) About 10 min. keep data into micro SD card and program display Result heavy metal.
- 5) Display value.
- 6) End program.

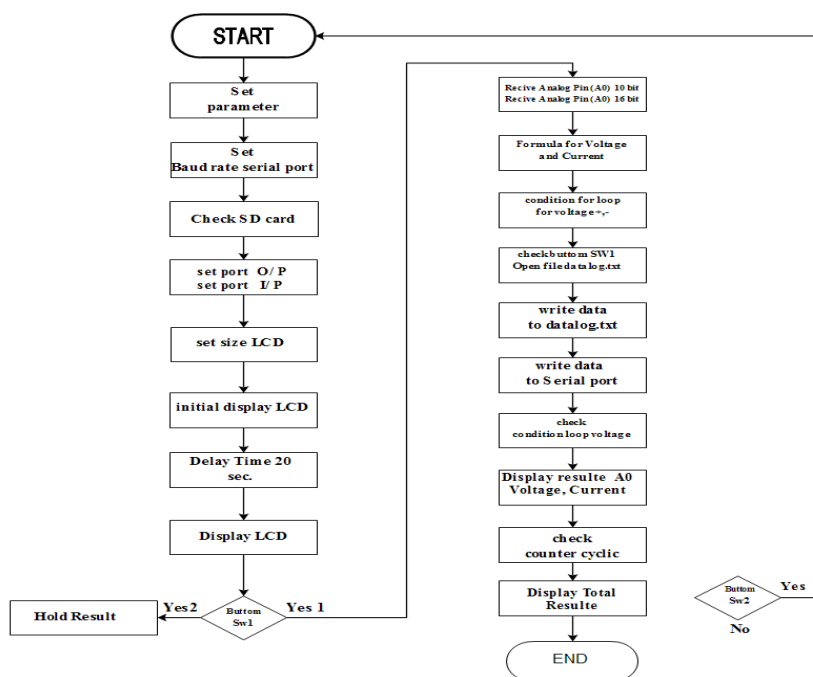


Fig. 2 Step for program

Step for study electrode efficiency

1. Calibration Standard curve from stock standard solution of lead (Pb), cadmium (Cd) and copper (Cu)
2. Testing electrode on standard solution of lead (Pb), cadmium (Cd) and copper (Cu)
3. Testing electrode on mix standard solution of lead (Pb), cadmium (Cd) and copper (Cu) (Fig. 3)
4. Voltage -1.7 to 1.7 V
5. Fix Time
6. Collected water sample in real sample from local environment, tap water

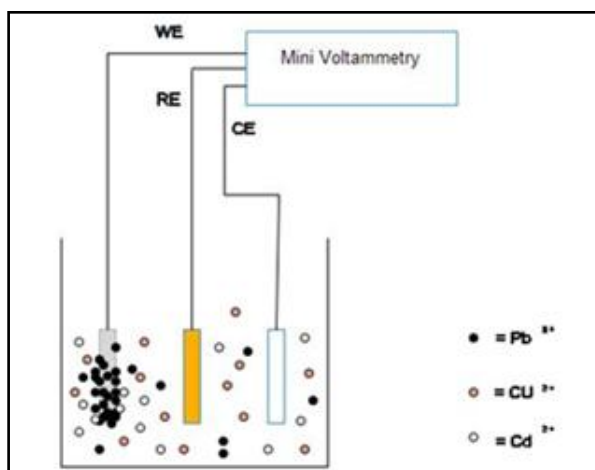


Fig.3 Show electrode testing on mix standard solution of lead (Pb), cadmium (Cd) and copper (Cu)

### III. Results and Discussions

The results of the determination of Pb, Cd and Cu in Standard solution sample and Tap water from the linearity between the metal concentration and the peak current, we can estimate the detection sensitivity of the electrode. Fig. 4 shows the peak current of Pb Cd and Cu concentration, respectively. The slopes of the linearity were determined to be  $9.03 \pm 0.15 \mu\text{A} / \mu\text{g cm}^2$ . The detection limits of  $0.09 \mu\text{g L}^{-1}$  for Pb,  $0.15 \mu\text{g L}^{-1}$  for Cd and  $0.13 \mu\text{g L}^{-1}$  for Cu. The high sensitivity and good reproducibility of the nontoxic gold wire, platinum and silver wire electrode make it possible to apply the electrode to a portable system for a trace metal analysis.

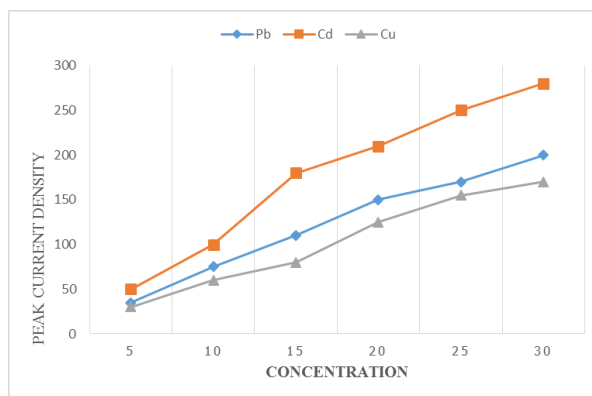


Fig.4 Peak current of Pb Cd and Cu concentration

The determination of determination of Pb(II), Cd(II) and Cu(II) were carried out in real sample from our local environment, tap water. The water sample were collected and adjusted to p H 1.5 to 2.0 without any other pretreatment. The standard addition method was used and know amounts of lead cadmium and copper was spiked to the water sample in triplicate (n=3) according the portable voltammetry procedure described in experimental section (Table2) summarizes the recovery of the results in table 2 and relative error in table 1 indicate good recoveries between 97% to 101.2%. The good values observed in the recovery procedure show that the proposed method is suitable for the determination of of Pb(II), Cd(II) and Cu(II) in real water sample.

Table 1: The results of the determination of Pb, Cd and Cu in Standard solution and Tap water

sample	Portable Voltammetry	Comparative method ( GFAAS)	Error (%) <sup>a</sup>
<b>Pb(II) (<math>\mu\text{g L}^{-1}</math>)</b>			
Tap water	0.831 $\pm$ 0.008	0.931 $\pm$ 0.002	2.428
Standard solution Pb5 $\mu\text{g L}^{-1}$	4.872 $\pm$ 0.008	4.972 $\pm$ 0.008	2.053
<b>Cd(II) (<math>\mu\text{g L}^{-1}</math>)</b>			
Tap water	0.342 $\pm$ 0.008	0.312 $\pm$ 0.002	-8.771
Standard solution Cd 5 $\mu\text{g L}^{-1}$	5.125 $\pm$ 0.008	4.848 $\pm$ 0.008	-5.405
<b>Cu (II) (<math>\mu\text{g L}^{-1}</math>)</b>			
Tap water	0.642 $\pm$ 0.009	0.531 $\pm$ 0.002	7.632
Standard solution Cu 5 $\mu\text{g L}^{-1}$	4.765 $\pm$ 0.008	4.866 $\pm$ 0.008	2.119

<sup>a</sup> [(Portable Voltammetry method - Comparative method)/ Comparative method]x 100

Table 2: The Recovery of the Results

sample	Added $\mu\text{g L}^{-1}$	Found by portable voltammetry			Found by GFAAS			Recovery (%)		
		Pb(II)	Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)
Tap water		0.831	0.342	0.642	0.931	0.312	0.531	-	-	-
	5	5.621	5.311	5.582				99.8	98.8	96.7
	10	11.332	14.212	13.261						
sample		4.872	5.125	4.765	4.972	4.848	4.866	-	-	-
	5	9.324	18.543	8.721				97.9	101.2	100.8
	10	14.721	26.541	16.564				98.6	97.3	98.7

Summarize for Electroanalytical application for the trace determination of metals in table 3

Table 3 Electrochemical techniques

Sample	Analyte technique	Voltammetric electrode	Working	Compared	References
Standard solution	Pb Cd Zn	SV	Carbon-electrode	BAS	[5]
Tap water, human hair	Pb Zn	ASV	Bismuth electrode	AAS	[6]
River water	Pb Cd Zn	ASV	Bi- CNT electrode	ICP-MS	[7]
Standard solution	Pb Cd Zn	ASV	Graphite electrode	DPV	[8]
Lake, Water sample	Pb Cd Zn	PAS	CNT- electrode	AAS	[9]
Herb	Pb Cd Zn	SIA-ASV	CNT-electrode	ICP-AES	[10]
Black tea	Pb	PSA	Carbon-electrode	AAS	[11]
Tap water	Pb Cd	SWASV	Carbon fiber electrode	Unmodified	[12]
Tap water	Cd Pb Cu Zn	ASV	Mercury electrode	AAS	[13]
Standard solution	Pb	ASV	Glassy carbon electrode	AAS	[14]
Rice	Pb Cd	SWASV	Graphene electrode	EIS	[15]
Sugar, Coffee and tea	Cu	SW-ASV	Mercury electrode	AAS, ICP-AES	[16]
Water sample	Pb	CV	Carbon electrode	EIS	[17]
Standard solution	Pb Cu	SWASV, CV	Gold electrode	Commercial	[18]
Standard solution	Pb Cd Cu	SWASV, CV	Gold wire electrode	GFAAS	This work
Tap water					

#### IV. Conclusion

In this study, we demonstrated the portable voltammetry that used gold wire, platinum wire and silver wire for working electrode, reference electrode and counter electrode respectively. The electrode can be easily prepared and showed a good analytical response for lead (Pb), Cadmium (Cd) and copper (Cu) in standard solution and tap water. The portable heavy metal meter is easily taken, used and low cost, which is a feature useful for monitoring the lead (Pb), Cadmium (Cd) and copper (Cu) in tap water, waste water, drinking water and herbal tea.

#### Acknowledgements

We are grateful to thank Faculty of Science, Burapha University and Institute of Marine Science, Burapha University for supporting.

#### References

- [1] E.B. Grzesik, and A.J. Kolon, Leaching of cadmium and lead from dried fruits and fruit teas to infusions and decoctions. *Food Composition and Analysis Journal*, 21, 2008, 326–331.
- [2] F.K. Gorur, R. Keser, N. Akcay, S. Dizman, and N.T. Okumusoglu, Radionuclides and heavy metals concentrations in Turkish market tea. *Food control*, 22(12), 2011, 2065–2070.
- [3] R.F. Milania, M.A. Morganoa, and C. Cadoreb, Trace elements in *Camellia sinensis* marketed in southeastern Brazil: Extraction from tea leaves to beverages and dietary exposure. *LWT - Food Science and Technology*, 68, 2016, 491–498.
- [4] P.B. Ning, C.M. Gong, Y.M. Zhang, K.K. Guo, and J.A. Bai, *Lead, cadmium, arsenic, mercury and copper levels in Chinese Yunnan Pu'er tea*. Food Additives & Contaminants. Part B, Surveillance, 4(1), 2011, 28–33.
- [5] A. Krolicka, R. Pauliukait, I. Svancara, R. Metelkac, A. Bobrowskia, A. Norkusb, K. Kalcherd, and K. Vytřas, Bismuth-film-plated carbon paste electrodes. *Electrochemistry Communications*, 4, 2002, 193-196.
- [6] G. Kefala, A. Economou, A. Voulgaropoulos, and M. Sofoniou, A study of bismuth-film electrodes for the detection of trace metals by anodic stripping voltammetry and their application to the determination of Pb and Zn in tapwater and human hair. *Talanta*, 61, 2003, 603-610.
- [7] G. Hwang, W.K. Han, J.S. Park, and S.G. Kang, Determination of trace metals by anodic stripping voltammetry using a bismuth-modified carbon nanotube electrode. *Talanta*, 76, 2008, (2), 301–308.
- [8] V. Rehacek, I. Hotovy, M. Vojs, and I. Mika, (2008) Bismuth film electrodes for heavy metals determination, *Microsyst Technol*, 14, 2008, 491–498.
- [9] C.R.T. Tarleya, V.S. Santosa, B.E.L. Baêtaa, A.C. Pereirab, and L.T. Kubota, Simultaneous determination of zinc, cadmium and lead in environmental water samples by potentiometric stripping analysis (PSA) using multiwalled carbon nanotube electrode. *Hazardous Materials*, 169, 2009, 256–262.
- [10] U. Injanga, P. Noyroda, W. Siangprohb, W. Dungchaia, S. Motomizuc, and O. Chailapakulad, (2010) Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbonnanotubes electrodes. *Analytica Chimica Acta*, 668, 2010, 54–60.
- [11] J. Guo, Y. Chai, R. Yuan, Z. Song, and Z. Zou, (2011) Lead (II) carbon paste electrode based on derivatized multi-walled carbon nanotubes: Application to lead content determination in environmental samples. *Sensors and Actuators B*, 155, 2011, 639–645.
- [12] S. Anandhakumar, and J. Mathiyarasu, In situ bismuth film modified carbon fiber microelectrode for nanomolar detection of cadmium and lead. *Indian journal of chemistry*, 51A, 2012, 699-703.
- [13] J. Raj, A. Raina, Mohineesh and T.D. Dogra, Direct Determination of Zinc, Cadmium, Lead, Copper Metal in Tap Water of Delhi (India) by Anodic Stripping Voltammetry Technique. *EDP Sciences*, 2013
- [14] L.T. Tufa, K. Sirajz, and T.R. Soreta, Electrochemical Determination of Lead Using Bismuth Modified Glassy Carbon Electrode. *Russian Journal of Electrochemistry*, 49, 2013, 59–66.
- [15] Z. Wang, H. Wang, Z. Zhang, and G. Liu, Electrochemical determination of lead and cadmium in rice by adisposable bismuth/electrochemically reduced graphene/ionic liquid composite modified screen-printed electrode. *Sensors and Actuators B* 199, 2014, 7–14.
- [16] K. Hevia, V. Arancibia, and C.R. Romo, Levels of copper in sweeteners, sugar, tea, coffee and mate infusions. Determination by adsorptive stripping voltammetry in the presence of  $\alpha$ -lipoic acid, *Microchemical Journal*, 119, 2015, 11–16.
- [17] F.E. Salih, A. Ouarzane, and M.E. Rhazi, Electrochemical detection of lead (II) at bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode. *Arabian Journal of Chemistry*, 2015.
- [18] W. Wan, Q. Sun, H. Li, F. Sun, N. Hu, and P. Wang, Screen-printed gold electrode with gold nanoparticles modification for simultaneous electrochemical determination of lead and copper. *Sensors and Actuators B*, 209, 2015, 336–342.