

## Portable Voltammetric Device for Detecting Heavy Metal Contamination

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**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 cyclic voltammetry. The electrode that used gold wire, silver wire and platinum wire for working electrode, counterelectrode and reference electrode respectively. The electrode can be easily prepared and showed a good analytical response was linear in the range of  $10 \mu\text{g L}^{-1}$  to  $50 \mu\text{g L}^{-1}$ . Successive cyclic voltammograms of gold electrode and scan start voltage  $-1.30 \text{ V}$  to  $1.3 \text{ V}$  at room temperature. The high sensitivity and good reproducibility of the nontoxic gold wire, platinum wire and silver wire electrode make it possible to apply the electrode to a portable system for a trace metal analysis. The portable voltammetric device for detecting heavy metal contamination is easily taken, used and low cost. Finally, the portable voltammetric device for detecting heavy metal contamination was applied for the analysis of lead cadmium and copper with satisfactory results.

**Keywords:** Heavy metal, Electrochemical techniques, Voltammetric techniques, Microcontroller, Cyclic Voltammetry

### 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. Summarize for Electroanalytical application for the trace determination of metals in Table 1

**Table 1** Electrochemical techniques

Sample	Analyte techniqueelectrode	Voltammetric	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	CV	Gold wire electrode	GFAAS	This work
Water sample					

In this present study, the portable voltammetric device for detecting heavy metal contamination in Standard solution 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 cure were compare from graphite furnace atomic absorption spectrometer (GFAAS).

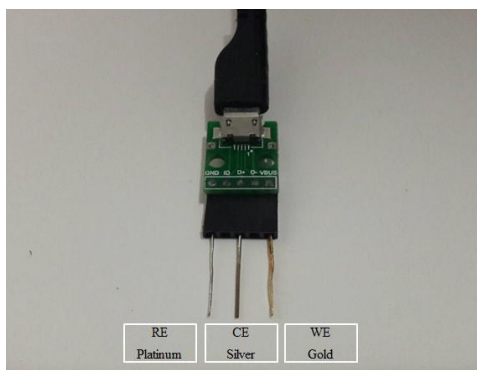
### 2.2 Preparation the electrode

A three-electrode was employed for Portable voltammetric device for detecting heavy metal. (cyclic voltammetry). A gold wire was used as the working electrode. A silver wire and a platinum wire were used as the counter electrode and reference electrode (Figure 1)

2.2.1 Platinum wire cleaning, Rinse platinum with deionized water (DI water) thoroughly and immerse it in 10%  $\text{HNO}_3$  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%  $\text{HNO}_3$  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%  $\text{HNO}_3$  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.



**Figure 1A** three-electrode was employed for Portable voltammetric device for detecting heavy metalcontamination (cyclic voltammetry)

### 2.3 Design and circuit built on a printed circuit board (PCB) for Portable voltammetric device for detecting heavy metal contamination (Figure 2)

#### Block a, Variable digital voltage

This circuit can provide currents up to 100mA. The working and circuit is explained below. Here we are going to take the voltage provided at the OUTPUT terminal and feed it into one of ADC channels of Arduino. After conversion we are going to take that DIGITAL value and we will relate it to voltage and show the result in 16\*4 display. This value on display represents the variable voltage value.

The UNO ADC is of 10 bit resolution (so the integer values from (0-(2<sup>10</sup> 1023)). This means that it will map input voltages between 0 and 5 volts into integer values between 0 and 1023. So for every (5/1024= 4.9mV) per unit.

#### Block b, Negative voltage and OP-Amp inverting

Simple Negative Voltage Converter The majority of applications will undoubtedly utilize the ICL7660 for generation of negative supply voltages. Figure below shows typical connections to provide a negative supply for Op-Amp inverting circuit will make variable negative voltage

#### Block c, Switching pole circuit

In circuit use transistor make not gate circuit for Switching Positive voltage and Negative voltage. Programming control at digital output pin

#### Block d, Current sensor circuit and ADC 16Bit I2C (MCP3425)

Use ic CA3130 This simple micro ampere meter circuit can help in measuring small currents. The output voltage of the opamp CA3130 is proportional to the measured current. By feedback resistors through. Ic MCP3425 convert Analog signals to Digital signals by I2C for Addition Arduino.

#### Block e, Microcontroller Arduino uno r3

Arduino Uno r3 is a microcontroller board based on the ATmega328P. Arduino is easy to learn microcomputer system. Many engineering students are using it in their projects and professionals also. Because it is ready to use board.

#### Block f, Display LCD 16X4 Module

Display LCD 16X4 Module are using a 16×4 Character LCD so we have 4 lines of 16 characters each available. The I2C LCD module is connected to 4 pin. Is VCC ,GND, SDA and SCL from the Arduino are connected to the breadboard.

#### Block g, Micro SD card Module

This is a Micro SD module. It is compatible with SD card (commonly used in Mobile Phone) which is the most tiny card in the market. SD module has various applications such as data logger, audio, video, graphics. This module will greatly expand the capability an Arduino can do with their poor limited memory.

This module has SPI interface and 5V power supply which is compatible with Arduino UNO/Mega. The Pinout is fully compatible

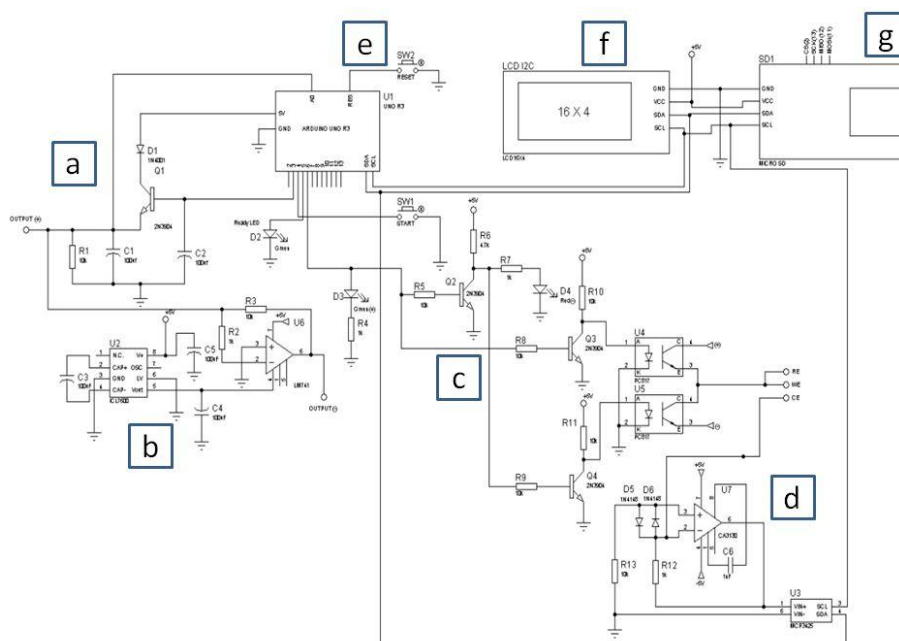
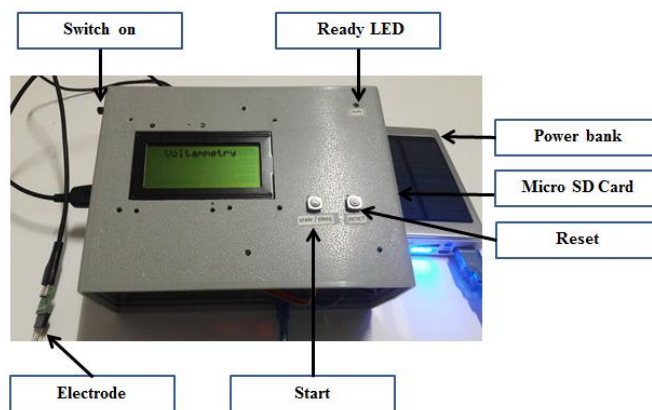


Figure 2 Portable voltammetric device for detecting heavy metal contamination circuit

**2.4 Invent auto variable power supply and voltmeter ammeter keep data to micro SD**

Experiment step for Invent meter, voltmeter ammeter and power supply  
(Portable voltammetric device for detecting heavy metal contamination, Figure 3)

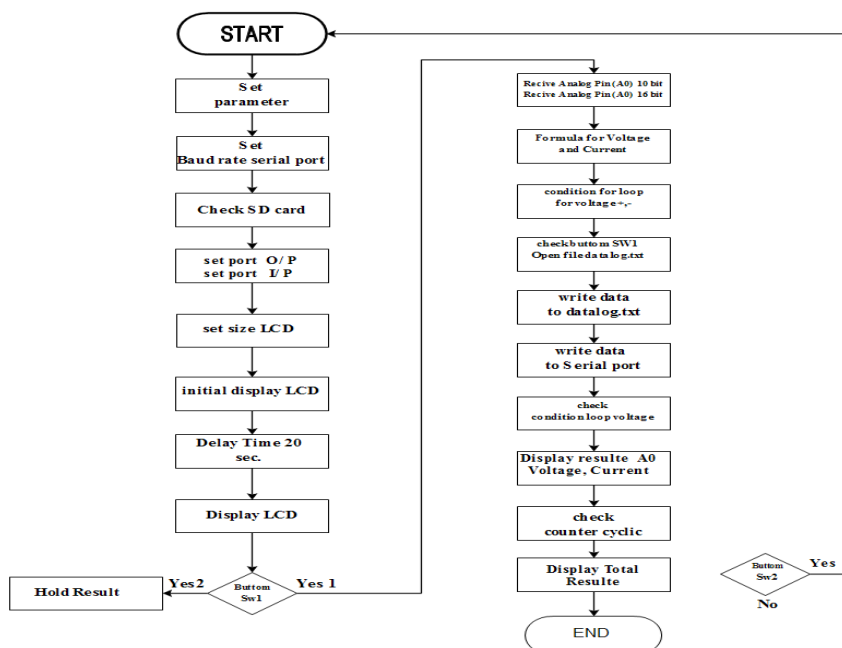
1. Make variable power supply circuit 0-5V by Arduino IDE (microcontroller).
2. Add A to D 16 bit module 16 Bit Analog to digital with I<sup>2</sup>c (MCP3425)
3. Make negative power supply circuit -5V by IC ICL7660
4. Make inverting OP-AMP for variable negative power supply
5. Make program control power supply -1.30 V to 1.30 V by Arduino IDE.
6. Make program memory value to SD card.
7. Display value to LCD display.



**Figure 3** Portable voltammetric device for detecting heavy metal contamination

The step for the program on Portable voltammetric device for detecting heavy metal contamination (Portable cyclic voltammetry) (Figure 4)

1. Connect USB electrode dip electrode in sample.
2. Start program to push button switch "start"
3. Voltammetry portable will scan start voltage -1.30 v to 1.3v
4. About 10 min. keep data into micro SD card and program display Result heavy metal.
5. Display value.
6. End program.



**Figure 4** The step for the program on Portable voltammetric device for detecting heavy metal contamination

**2.5 Program Portable voltammetric device for detecting heavy metal contamination**

```

( Arduino IDE 1.6.8 )
#include <MCP342X.h>
#include <Wire.h>
#include <LiquidCrystal_I2C.h>
#include <SD.h>
// MCP3425 I2C address is 0x68(104)
#define Addr 0x68
LiquidCrystal_I2C lcd(0x3F,16, 4);
const int chipSelect = 2;
int dataString = 0;
//***** parameter voltage*****//
int voltageadjust =44; //starting initial variable output
float volts = 0.0;
float Current = 0.0;
float tpb = 0.0;
float tcu = 0.0;
float tcd = 0.0;
//**** parameter voltage loop ****//
int a=0,i=0,j=0;
//***** parameter button switch pin 4 output pin 5 ****//
int buttonPin = 4;
int controlOut = 5;
int ledPin = 6;
int ledState = LOW;
int lastState = HIGH;
int StateOut = HIGH;
void setup()
{
// Initialise I2C communication as MASTER
Wire.begin();
// Start serial communication and set baud rate = 9600
Serial.begin(9600);
// Start I2C Transmission
Wire.beginTransmission(Addr);
// Send configuration command
// Continuous conversion mode, 12-bit resolution
Wire.write(0x10);
// Stop I2C Transmission
Wire.endTransmission();
delay(300);
while (!Serial)
{ ; }
Serial.print("Initializing SD card...");
// make sure that the default chip select pin is set to
// output, even if you don't use it:
pinMode(2, OUTPUT);
// see if the card is present and can be initialized:
if (!SD.begin(chipSelect)) {
Serial.println("Card failed, or not present");
lcd.print(" Card failed ");
// don't do anything more:
return;
}
Serial.println("card OK.");
pinMode(3,OUTPUT);//PWM output pin
pinMode(buttonPin,INPUT);//button Start
pinMode(controlOut,OUTPUT);//OUTPUT control PC817
pinMode(ledPin,OUTPUT);

```

```
lcd.begin();//number of characters on LCD
// Print a logo message to the LCD.
lcd.print(" Voltammerty");
lcd.setCursor(0, 1);
delay (2000);
lcd.clear();
lcd.print("Volt=");//printing name
lcd.setCursor(2, 1);
lcd.print("I =");//printing name
}
void loop()
{
unsigned int data[2];
// Start I2C Transmission
Wire.beginTransmission(Addr);
// Select data register
Wire.write(0x00);
// Stop I2C Transmission
Wire.endTransmission();
// Request 2 bytes of data
Wire.requestFrom(Addr, 2);
// Read 2 bytes of data
// raw_adc msb, raw_adc lsb
if(Wire.available() == 2)
{
data[0] = Wire.read();
data[1] = Wire.read();
}
// Convert the data to 12-bits
int raw_adc = (data[0] & 0x0F) * 256 + data[1];
if(raw_adc > 2047)
{
raw_adc -= 4096;
}
int buttonState = digitalRead(buttonPin);
if(buttonState == LOW && buttonState!=lastState)
{
if(StateOut==HIGH)
{
StateOut = LOW;
}
else
StateOut = HIGH;
}
}
digitalWrite(controlOut,StateOut);
lastState = buttonState;
delay(20);
float VOLTAGEVALUE = (analogRead(A0));//read ADC value at A0
if(ledState==LOW)
{
VOLTAGEVALUE = ((VOLTAGEVALUE*5)/1024);//converting digital value to voltage
}
else
{
VOLTAGEVALUE = -((VOLTAGEVALUE*5)/1024);//converting digital value to voltage
}
float DCvalue = raw_adc;
volts = (DCvalue)-10;
```

```
Current = volts;
{
if ( StateOut == LOW && dataString<1312)
{
File dataFile = SD.open("datalog.txt", FILE_WRITE);
dataFile.print(dataString);
dataFile.print("\t ");
dataFile.print(VOLTAGEVALUE, 4);
dataFile.print("\t ");
dataFile.println(Current, 4);
dataFile.close();
// print to the serial port too:
Serial.println(dataString);
dataString++;
//delay(30);
}
lcd.setCursor(5, 0);//go to position 9 on LCD
lcd.print(VOLTAGEVALUE);
lcd.setCursor(11, 0);
lcd.print("V");
lcd.setCursor(-15,5);//go to position 9 on LCD
lcd.print(Current,4);
}
analogWrite(3,voltageadjust);//provide PWM at PIN3
if(StateOut == LOW)
{
if(i<65)
{
Serial.print("Step No:")
Serial.println(i);
Serial.print(" AIN0: ");
Serial.print(analogRead(A0));
Serial.print(" \tVoltage: ");
Serial.print(VOLTAGEVALUE, 4);
Serial.print("V");
Serial.print("\tCurrent: ");
Serial.print(Current, 4);
Serial.println("uA");
delay(300);
voltageadjust++;
i++;
// delay(300);
}
else if(j<65)
{
Serial.print("Step No:")
Serial.println(j);
Serial.print(" AIN0: ");
Serial.print(analogRead(A0));
Serial.print(" \tVoltage: ");
Serial.print(VOLTAGEVALUE, 4);
Serial.print("V");
Serial.print("\tCurrent: ");
Serial.print(Current, 4);
Serial.println("uA");
delay(300);
voltageadjust--;
j++;
// delay(3000);
```

```

// Serial.println("*****");
}
else if(a<9)
{
Serial.println("-----");
Serial.print("a=");
Serial.println(a);
i=0;j=0;
//a++;
if(a>=0)
{
if (ledState == LOW)
{
ledState = HIGH;
}
else
{
ledState = LOW;
}
digitalWrite(ledPin,ledState)
}
a++;
}
if( a==9 && j==65 )
{
lcd.clear();
lcd.print( "Cyclic = 5 turn");
delay(1500);
}
}
delay(20);
}
***** END PROGRAM *****

```

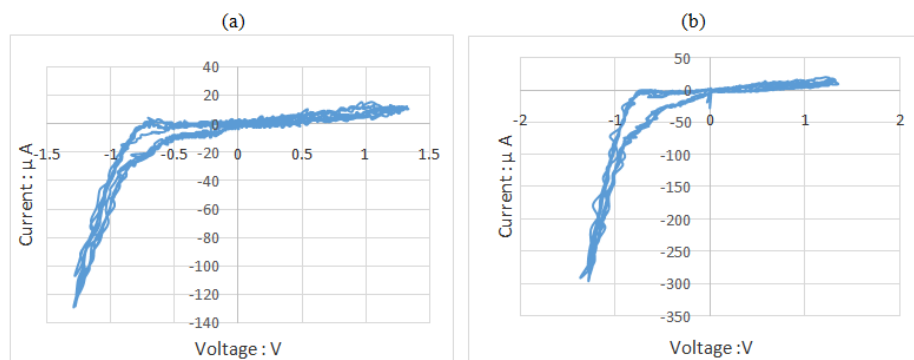
### 2.6 Testing for detect heavy metal in standard solution

To use the portable voltammetric device for detecting contamination in standard solution and sample water .

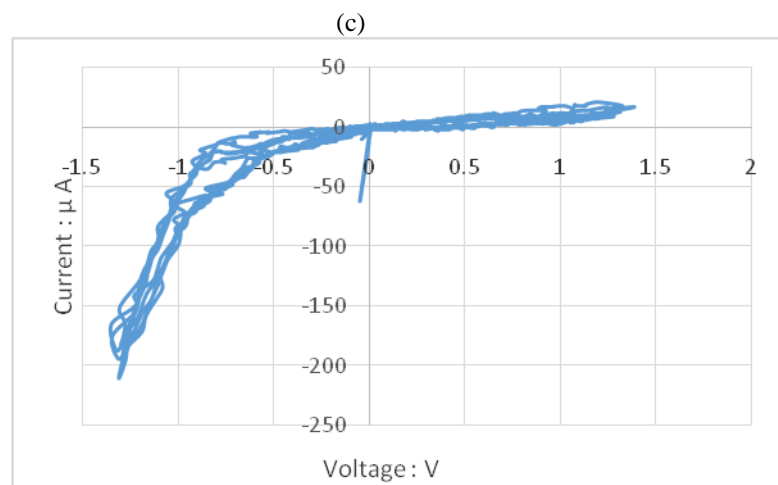
## III. RESULTS AND DISCUSSIONS

### 3.1 Effect of the supporting electrolyte, pH and Successive cyclic voltamograms

Influence of pH on the cyclic voltammograms for 20 - 100  $\mu\text{gL}^{-1}$  of Cd Pb and Cu at The portable voltammetric device in buffer solution. The influence of pH on the peak current of Cd Pb and Cu was studied in the pH range of 3.5 to 7.5 The results obtained show that the oxidation peak current increased with increased in pH from 3.5 to 7.5 ; however, the currents decreased when the pH further increased from 3.5 to 7.5. The decrease in peak current at higher pH values could be due to the formation of lead(Pb), cadmium(Cd) and copper (Cu). Among the various electrolytes (such as acetate buffer).The best results were obtained in acetate buffer media. Thus an electrode voltammetry of pH 5.5 was adopted as support electrolyte in the further studies. (Figure 5)





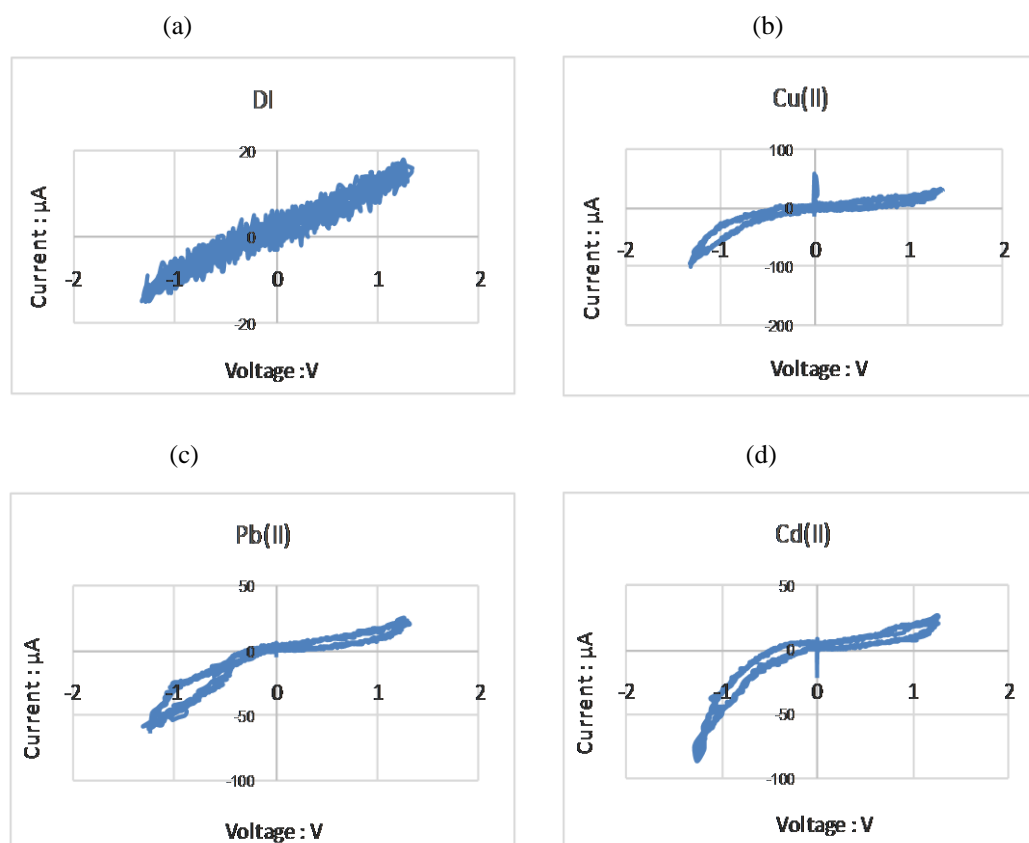


**Figure 5** Successive cyclic voltammograms of Lead (Pb) in acetate buffer (a) p H 3.5 (b) p H 5.5 and (c) p H 7.5

### 3.2 Analytical characteristics and Electrochemical behavior of the electrode voltammetry

The cyclic voltammetric was employed to investigate the electrochemical behavior on the gold wire silver wire and platinum wire electrode in 5.5 electrolyte (Figure 6)

Illustrates the responses obtained by cyclic voltammetry between -1.30 to 1.30 V at gold electrode.



**Figure6** Successive cyclic voltammograms (a) Deionized water (b) Copper(II)  $20\mu\text{g L}^{-1}$  (c) Lead(II)  $20\mu\text{g L}^{-1}$  (d) Cadmium(II)  $20\mu\text{g L}^{-1}$

3.3 The portable voltammetric device for detecting heavy metal contamination in standard solution and sample water

Successive cyclic voltammograms of following the potentiostatic recorded at room temperature. The electrode that used gold wire, silver wire and platinum wire for working electrode, counter electrode and reference electrode respectively. The electrode can be easily prepared and showed a good analytical response was linear in the range of  $10 \mu\text{g L}^{-1}$  to  $50 \mu\text{g L}^{-1}$ . Successive cyclic voltammograms of gold electrode and scan start voltage  $-1.30 \text{ v}$  to  $1.3 \text{ v}$  at room temperature. The portable voltammetric device for detecting copper (Cu) (Figure 7) cadmium (Cd) (Figure 8) and lead (Pb) (Figure 9) contamination.

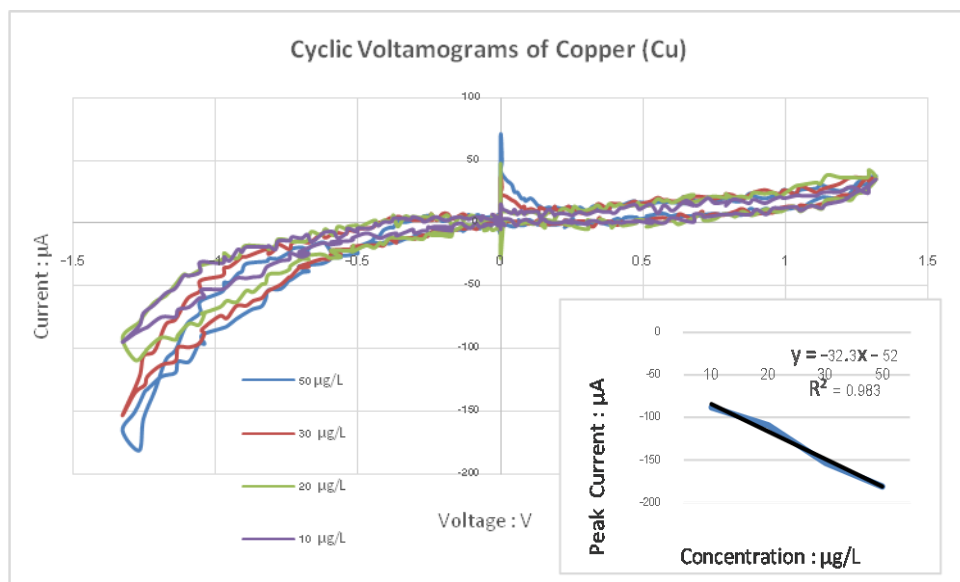


Figure 7 Cyclic voltammograms of Copper (Cu) following the potentiostatic recorded at room temperature

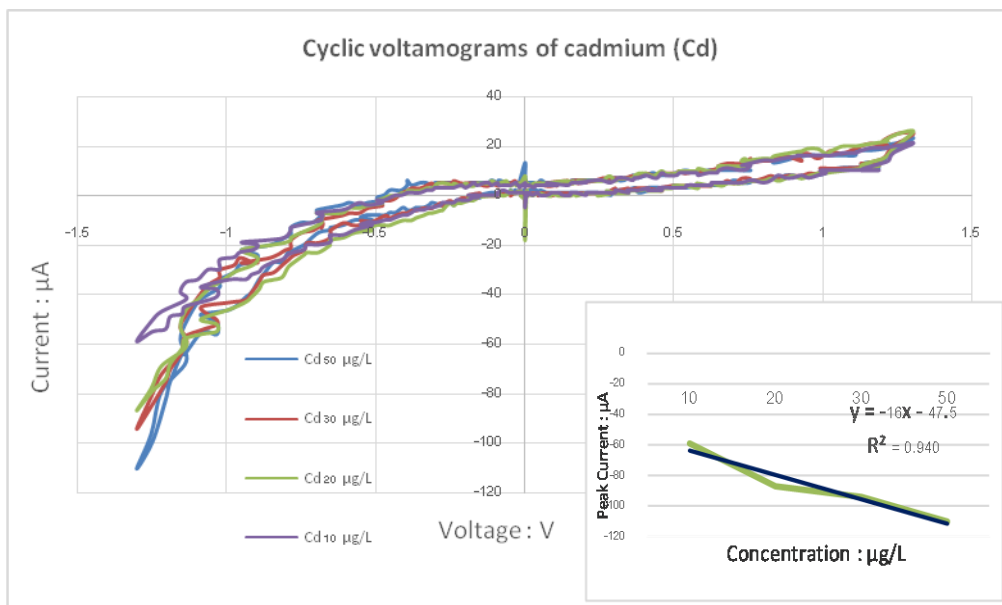


Figure 8 Cyclic voltammograms of cadmium (Cd) following the potentiostatic recorded at room temperature

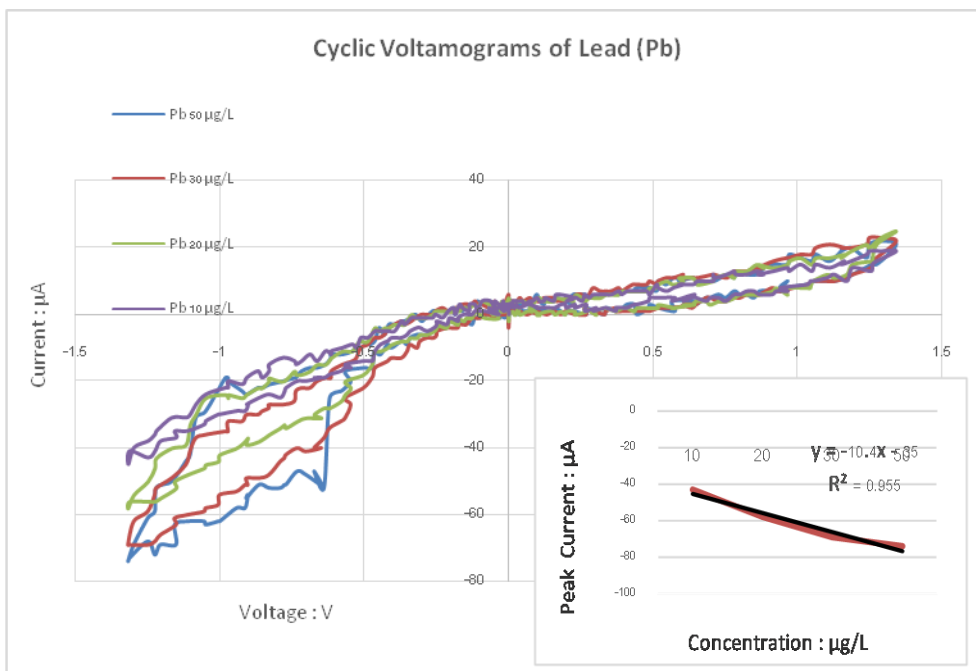


Figure 9 Cyclic voltammograms of Lead (Pb) following the potentiostatic recorded at room temperature

3.4 Linearity

Form the linearity between the metal concentration and the peak current, we can estimate the detection sensitivity of the electrode. (Figure 10 show the peak current against the Cd Pb and Cu concentrations)

The metal concentration deposited on the gold electrode increases with an increasing accumulation time. Therefore, as the accumulation time increases, the peak current is enhanced, which leads to an increase in the slope of the linear relationship between the peak current is significantly influenced by the portable voltammetric device for detecting heavy metal contamination.

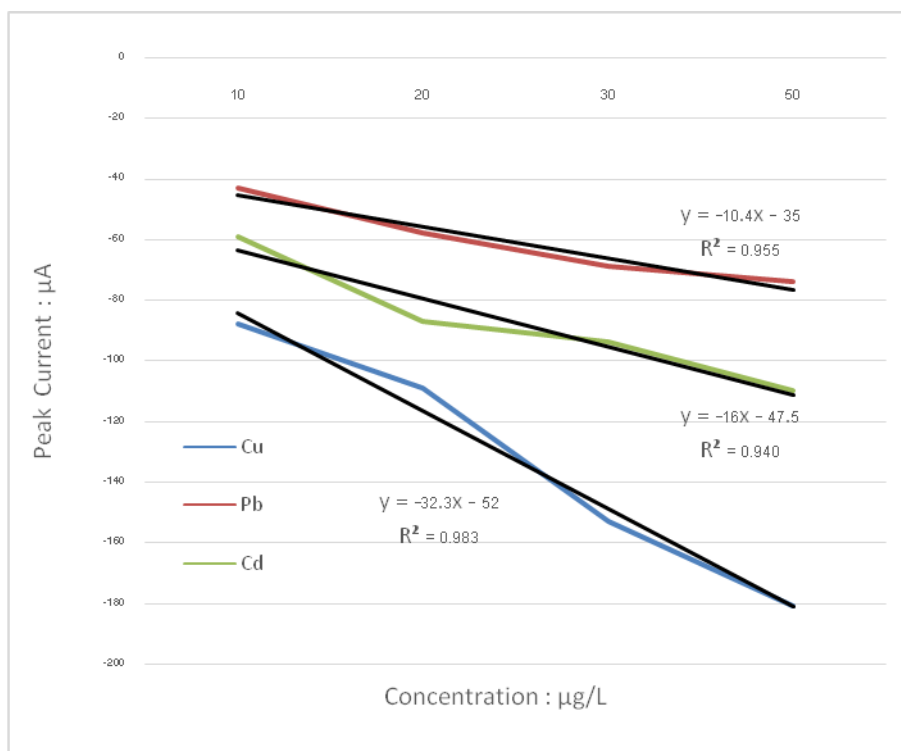


Figure 10 Dependency of the peak current on the concentration of (a) Cd, (b) Pb and (c) Cu

#### IV. CONCLUSION

In this study, we demonstrated the portable voltammetric device for detecting heavy metal contamination that used gold wire, silver wire and platinum wire for working electrode, counter electrode and reference 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. The portable voltammetry device is easily taken, used and low cost, which is a feature useful for monitoring the lead (Pb), Cadmium (Cd) and copper (Cu) in sample water, tap water, waste water and drinking water.

#### ACKNOWLEDGEMENTS

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

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