

## Development and Validation of Differential Pulse Anodic Stripping Voltammetric Method for Determination of Lead (II) in Ground Water Using a Pencil Graphite Electrode

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### Abstract

Inexpensive rapid, simple and an accurate voltammetric method based on pencil graphite electrode (PGE) was developed and validated for determination of lead (II) in water samples. Differential pulse voltammetry (DPV) applied to the anodic peak was used for the quantitative determination of lead (II) ions. Several parameters affecting the peak current and thus the sensitivity of the method, including concentration of supporting electrolyte, pH, scan rate, modulation amplitude, deposition time, and pencil grade were investigated. Linear calibration curve in range of 45  $\mu\text{M}$  to 1000  $\mu\text{M}$  was obtained. The limit of detection (LOD) and the limit of quantification (LOQ) were found to be 43.0  $\mu\text{M}$ , and 130  $\mu\text{M}$  respectively. The developed differential pulse voltammetric method using pencil graphite electrode was applied with good results to the quantitative determination of lead (II) in water samples. The results were compared with those results obtained using the ICP-OES method and no statistically significant difference between the methods was found.

**Keywords:** Differential Pulse Voltammetry (DPV); Lead, Pencil Graphite Electrode (PGE); Cyclic Voltammetry

### Introduction

Lead (Pb) is a very prevalent heavy metal [1]. That discovered early by the human being. It has widespread applications in automobile, ceramics, plastic and paint industries due to its singular properties such as malleable, ductile, soft, resistance to corrosion beside the low melting point. But lead poisoning is well known as a serious health problem. Once it has been accumulated in the body in a certain conditions may prove fatal [2]. Furthermore the United States Environmental Protection Agency (EPA) has reported the delay in children's physical or mental development, decreasing IQ, and increasing the risk of cancer [3-5]. Therefore monitoring of lead in the environment samples has become an essential requirement.

In the area of environmental analysis, a growing variety of low cost analytical sensors is always welcomed. Spectroscopic techniques in particular atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence spectrophotometer, inductively coupled plasma-mass spectrometry (ICP-MS), and Neutron activation analysis for trace-metal analysis was reported [6-9]. In spite of their advantages such as the sensitivity and their applicability to a large number of elements, these methods are expensive and complicated [10]. Corresponding to them the voltammetric techniques have more attractive features, including simplicity, low cost, with ease of miniaturization, minimal sample pretreatment [3,11].

The diversity of the electrodes materials gave the voltammetric methods a great importance and made them active, one of the widely used electrodes are carbon based materials such as glassy carbon (GC), carbon paste, or screen-printed electrodes [12-15]. Those methods need highly degree of training, preparation and care. Therefore alternative sources for the manufacture of carbon electrodes have been investigated and reported in the literature using pencil leads as electrodes [12,16-21]. The unique feature of the pencil graphite electrode is recognized not only by their cost but simplicity of fabrication and operation, furthermore there is renewable surface after each measurement, however the part of the used electrode can be easily removed and the new surface is readily available, and the surface polishing is generally not required prior to use. It's easily available as it is widely used for writing purposes as graphite pencil, it's also disposable and it's extremely low cost compared to other disposable electrode like screen-printed electrode. On the other hand, handling the pencil graphite electrode PGE is relatively easy, due to its shape, pencil graphite electrode is found more sensitive compared to Glassy Carbon Electrode GCE. (Greater sensitivity is due to the presence of porosity on the surface of pencil graphite electrode) [22-26].

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Different voltammetric methods using carbon electrodes for determination of lead were reported [12,27]. The possibility of applying 6B PDEs (Pencil Drawing Electrodes) for the anodic stripping voltammetric determination of trace concentrations of Pb was reported by Honeychurch [12]. The sensor was constructed by drawing of the electrode design onto a 0.5 mm PVC substrate (Cadillac Plastics, Swindon, UK) with a 6B pencil (Derwent Graphic, UK). The electrode was successfully used to detect the trace levels of Pb in environmental surface waters [12].

Voltammetric electrodes using graphite reinforced carbon (GRC) was proposed for the first time by Aoki et al. Due to the commercial availability of GRC as graphite and properties such as the low content of heavy metals impurities and high quality, controlled by the producer, in addition to the other electrochemical features of the carbon based electrodes have lead to the develop of this type of disposable sensors [27].

In the present work avoltammetric procedure using a disposable pencil graphite electrode (PGE) 7B for determination of lead (II) in environmental ground water samples was proposed. Parameters such as pH, ionic strength, scan rate, modulation amplitude, and type of pencil graphite lead were optimized. The method was successfully applied for analysis of lead (II) in water samples. The results were compared with those obtained using ICP-OES method.

### Experimental

#### Chemicals and reagents

All chemicals used in this study were analytical reagent grade, used without further purification, and supplied from Rasayan Laboratories (Mumbai, India), unless otherwise stated. Lead standard stock solutions were prepared by dissolving an appropriate mass of  $\text{Pb}(\text{CH}_3\text{COOH})_2$  in deionised water. For optimization of studies working standards were prepared by dilution of the standard stock solution with deionised water. Buffer solutions for optimization studies were prepared by dilution of acetic acid and sodium acetate to give a 0.10 M solution. This was fortified with sufficient KCl to give a 0.60 M solution. Environmental water samples (ground water) were obtained from south Khartoum "El- Farouk" city, Gedaref state, and bottled water samples purchased from local market. The mechanical cleaning of the working electrode was carried out using Aluminum oxide 60 G neutral (Type B) from MERCK (Darmstadt, Germany).

#### Instrument and apparatus

Voltammetric measurements were performed using an Autolab PGSTAT Metrohm connected to Nova 1.11.0 software (Netherlands). The cell used for the voltammetric measurements was obtained from Metrohm (Netherlands); A three-electrode system consisting of a disposable pencil graphite electrode PGE (Pencil graphite leads 7B, made in China) as working electrode purchased from a local market in the city of Khartoum in Sudan, a platinum electrode (Metrohm, Netherlands) as auxiliary electrode, and a Ag/AgCl/KCl (3M) (Metrohm, Netherlands) as reference electrode were used. A copper wire was coiled onto the tip of the pencil for supplying electrical contact. pH measurements was performed using a (PHS-3E pH-meter-China), Prior to the measurements the meter was calibrated with standard buffer solutions. Scanning electron microscopy measurement was done using a SEM (Zeiss Evo LS 10, Germany).

#### Preparation of PGE

The wood was stripped from the pencil, and then a certain length was cut, the bare pencil graphite electrode PGE was polished with alumina and then thoroughly washed twice with deionised water; the PGE was directly connected to the potentiostat cable through a clip. The electrical contact between the electrode and the instrument was realized through a copper wire wrapped at the other end of the pencil lead [27].

#### Electrochemical measurements

Voltammetric measurements were carried out in a glass voltammetric cell, before measurements, the mechanical cleaning of the PGE with aluminum oxide cleaning powder ( $\Omega$  Metrohm) to increase the activity of the surface of the electrode.

Cyclic voltammograms were initially recorded with plain solutions of 0.10 M acetate buffer, containing 0.6M KCl and then in the same solution containing 0.1 mM Pb. Degassing was achieved by purging with nitrogen for 2 minutes to eliminate oxygen reduction waves. A start and end potential of -1.1V vs. Ag/AgCl was used, with a stop potential of -0.2V vs. Ag/AgCl, Further studies were made by Differential Pulse Anodic Stripping Voltammetry using modulation amplitude 25 mV. The stripping voltammogram was measured over the potential range -1.0 V to -0.2 V vs. Ag/AgCl. The instrumental parameters applied were modulation amplitude, scan rate, and deposition time were 100 mV, 100 mV/s, and 95 seconds, respectively. All measurements were carried out at room temperature.

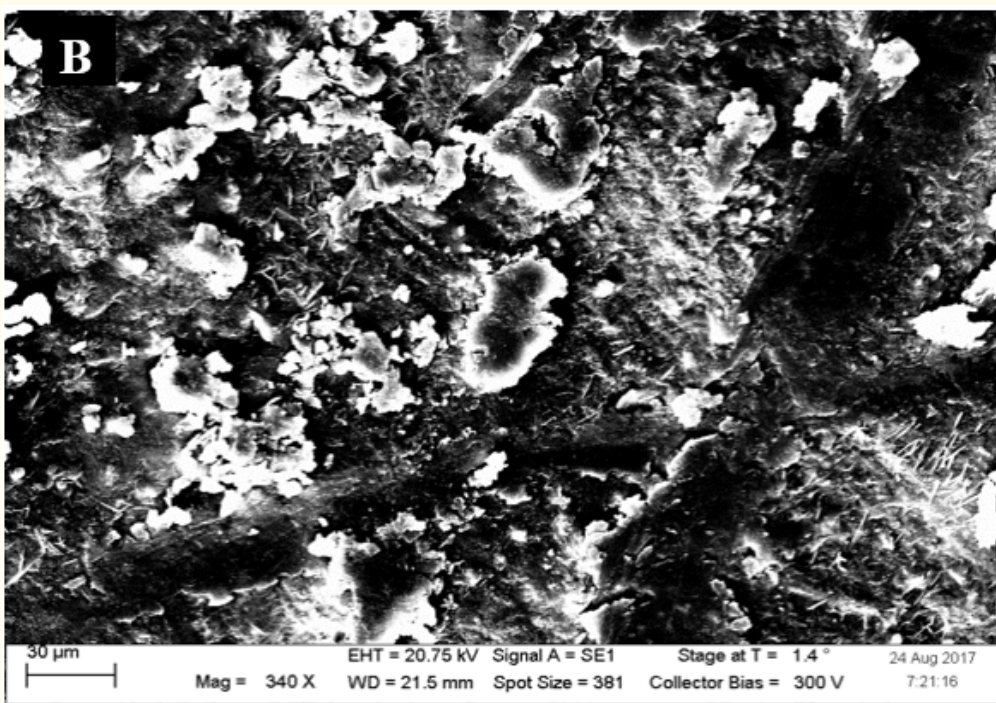
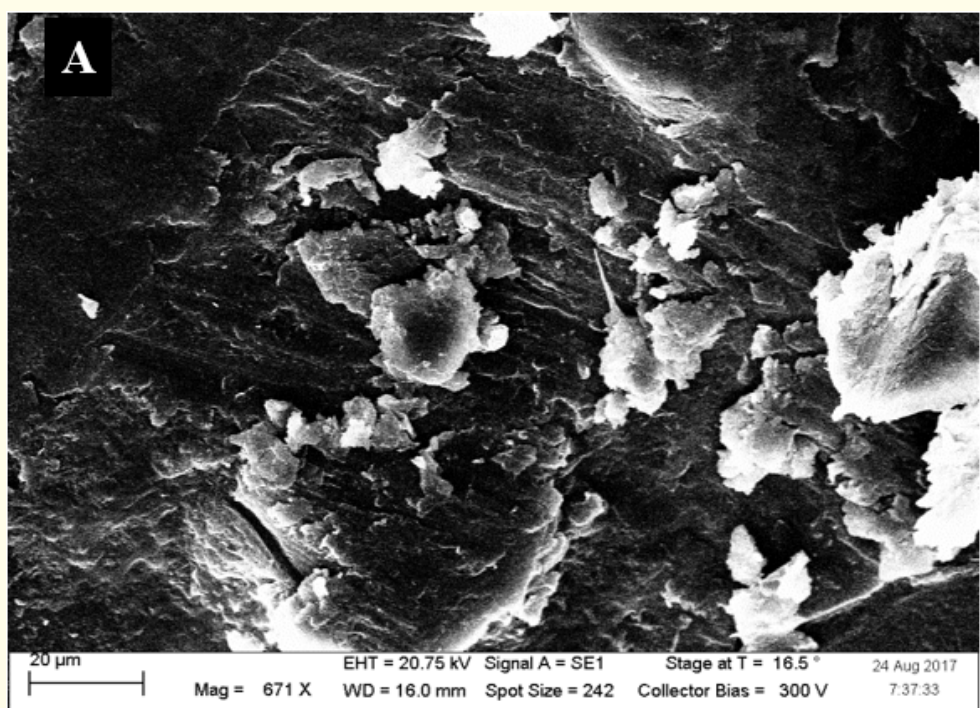
### Sample preparation procedure

Drinking water (Ground water) samples were collected from the South Khartoum and Gedaref State (Alssabagh and Wd-boshara localities) in Sudan, and Bottled water from the local Sudanese companies. The samples were kept in polycarbonate bottles at 4°C. The measurement procedure was directly applied to water samples without any sample preparation step.

### Results and Discussions

#### Scanning Electron Microscopy

Scanning electron microscopy SEM (Figure 1a-1c) investigations showed the surface of the Pencil graphite electrode PGE, It is obvious that the surfaces of the graphite electrodes exhibit high heterogeneity and are quite complex. The surface area was constituted from many cavities, grooves and stacked flakes at differing sizes constitute [12].



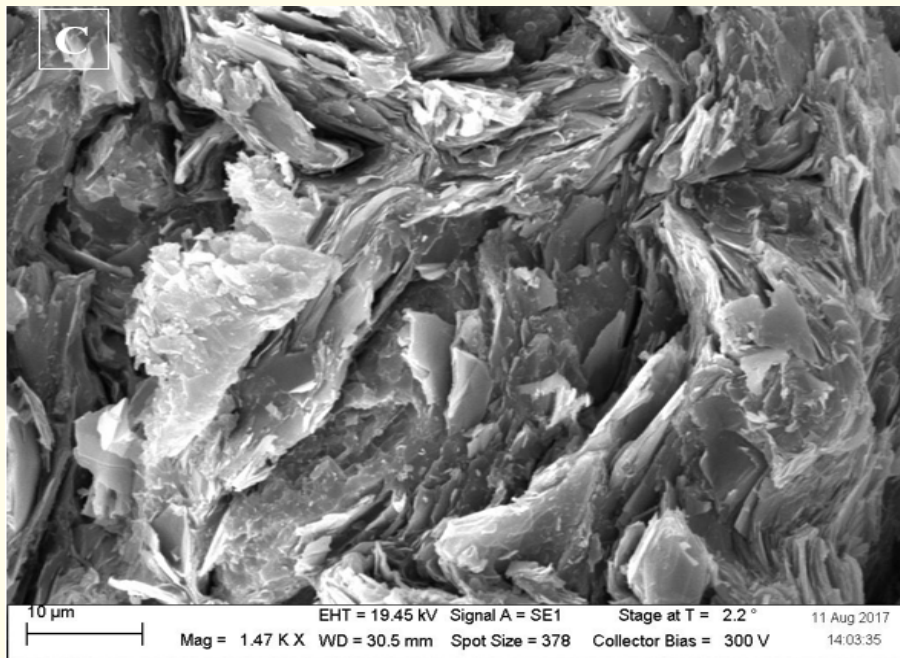


Figure 1: SEM image of a 7B bare pencil graphite electrode. (A) 30 times magnification, (B) 20 times magnification and (C) 10 times magnification.

#### Behavior of lead (II) ions at pencil graphite electrode

Cyclic voltammetric investigations of Pb (II) at pencil graphite electrode in 0.1M acetate buffer were characterized by a cathodic reduction peak on the initial negative scan resulting from the reduction of Pb (II) ions to Pb(0). Anodic peaks were obtained on the return to more positive scan indicated that Pb had been deposited as a thin film on the electrode surface. Figure 2A and figure 2B confirmed that.

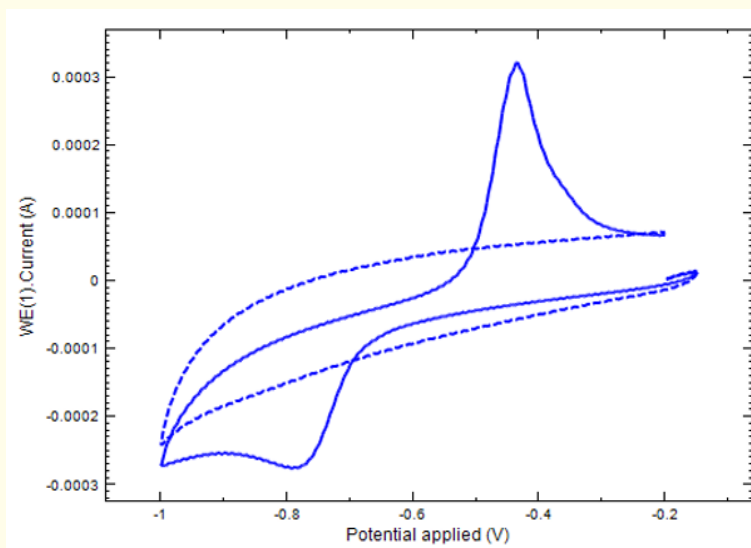
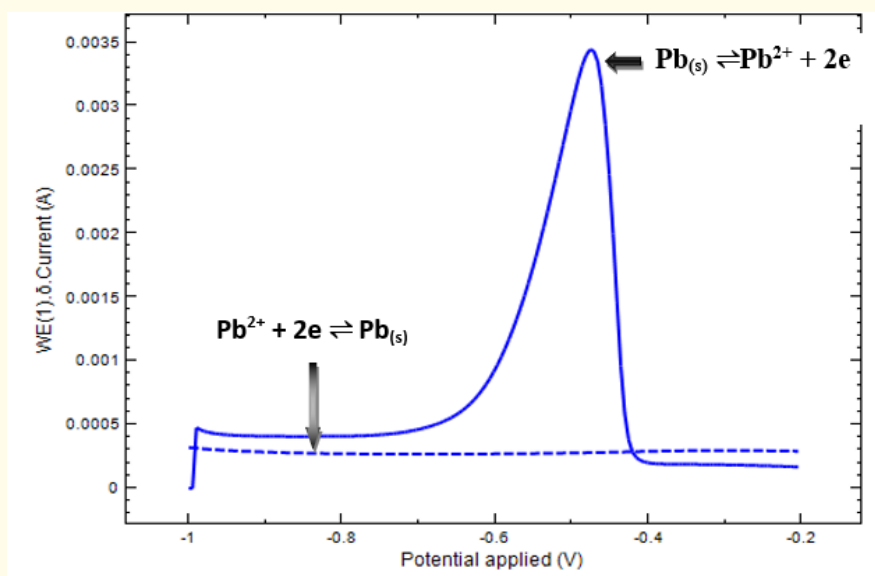


Figure 2A: Cyclic voltammograms obtained for the solution containing 0.1 M acetate buffer (pH 4.8), and 0.6M KCl at PGE (dashed line), and the same solution in addition to 0.1 mM of lead (solid line).

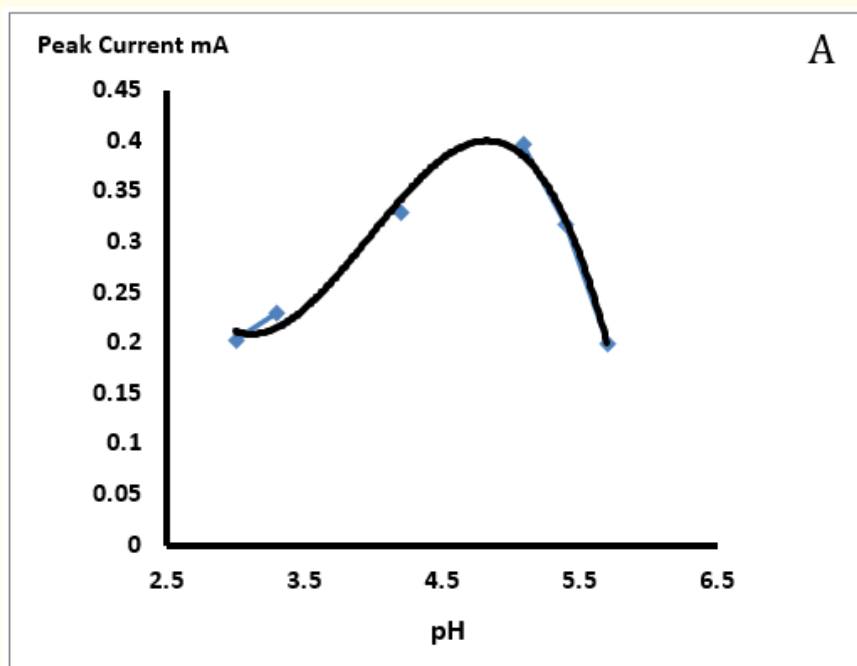


**Figure 2B:** Differential pulse anodic stripping voltammograms of acetate buffer 0.1M at pH (4.8), 0.6 M KCl, scan rate 100 mV/s, modulation amplitude 25 mV -(dashed line), and in addition to 0.1 mM of lead (solid line).

### Optimization conditions

#### Effect of pH, supporting electrolyte, or ionic strength

The chemical parameters such as pH, buffer concentration and supporting electrolyte or ionic strength are important solution parameters affecting the electrochemical reaction at the electrode surface [28]. Therefore, these parameters have been optimized. In order to investigate the effect of pH on the electrochemical responses of lead (II) at PGE, DPASV was carried out of a solution containing 0.1 mM lead (II) and 0.6 M KCl at pH values between 3.0 and 6.0 (Values outside of this range did not give a good reduction signal.) at a scan rate of 100 mV/s. It has been shown in figure 3A that both the potential and peak current of lead (II) reduction is affected by the solution pH. The relationship between the reduction peak potential and the pH is shown in figure 3B; a linear shift of  $E_{pa}$  towards negative potential with an increasing pH indicates that protons are directly involved in the reduction of lead (II). It obeys the following equation (Equation 1).



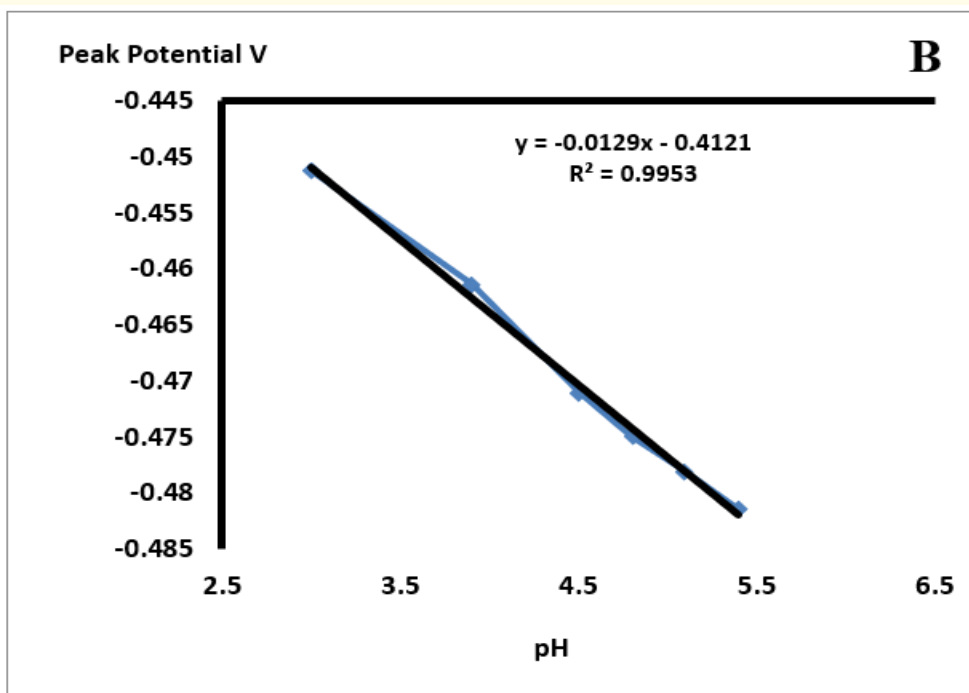


Figure 3: (A) Effect of pH on the peak current in 0.1M acetate buffer. Conditions: 0.1 mM Pb (II), 0.6M KCl, scan rate 100 mV/s, modulation amplitude 25 mV. And (B) Dependence of peak position of lead on the solution pH.

$$E_p(V) = -0.0129 \text{ pH} + (-0.4121) \quad (R^2 = 0.9953) \dots\dots\dots(1)$$

The effect of concentration of acetate buffer on peak current was also investigated in the range of 0.02 - 0.1M shown in figure 4. The peak current increased up to 0.1M. The concentration of acetate buffer was chosen as 0.10 M for subsequent studies.

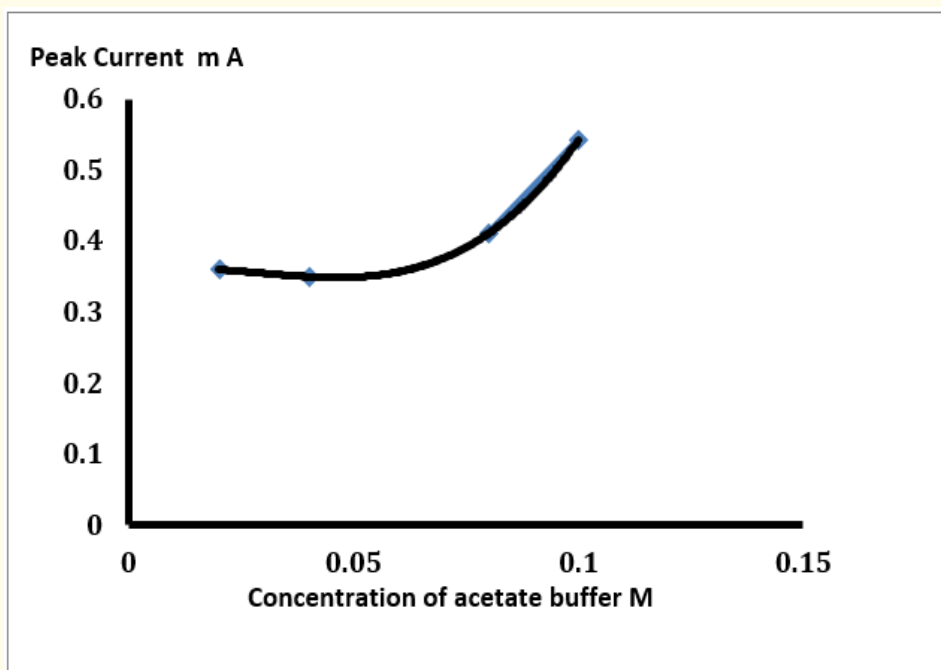
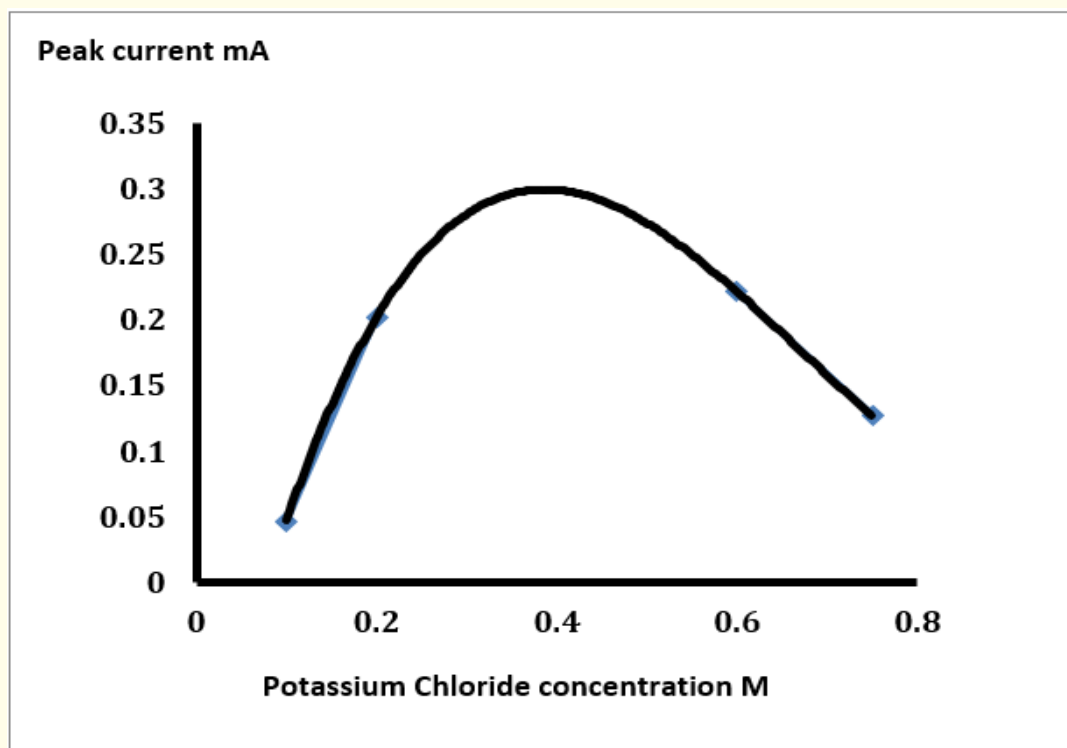


Figure 4: Dependence of the peak current on the acetate buffer concentration, other conditions is the same as in figure 2.

Ionic strength is a solution parameter that has an effect on the peak current and thus the sensitivity of the method [28]. Supporting electrolyte is used to facilitate electrical conduction in solution. They are applied to decrease the resistance of the solution and to eliminate electro migration effects and to provide a constant ionic strength in controlled potential experiments [10,29]. Different concentrations of potassium chloride were applied for this purpose and the results are shown in figure 5. The peak current increases with increasing potassium chloride concentration up to 0.6 M and then decreased and remained constant at higher values. Therefore, 0.6M potassium chloride was selected as optimum for the next measurements.



**Figure 5:** The effect of ionic strength on the peak current in 0.1 mM acetate buffer at pH 4.8. Other conditions are the same as in figure 2.

#### Effect of pencil grade

Pencils are graded on the European Letter Scale using H (hardness) and B (blackness) letters with a number representing degree of hardness or blackness. Pencil graphite can be considered as a composite electrode since it is composed of graphite, clays, and waxes as ingredients in varying amount to obtain different pencil grades [12]. Therefore, the effect of pencil grades on peak current utilizing H, B, 4B, 6B and 7B pencil leads was investigated and the results are presented in figure 6. From the figure it clear that as the proportion of graphite increased with increasing the percent of graphite. Consequently, 7B grade pencil lead was chosen as the working electrode material.

#### Effect of Scan Rate and Modulation amplitude

Scan rate and pulse amplitude are instrumental parameters affecting the peak current and consequently to the sensitivity [28]. Accordingly, the effect of scan rate and pulse amplitude was investigated and the results are presented in figures 7 and 8, respectively.

In order to see the effect of scan rate on the peak current of Lead (II) ions, cyclic voltammograms of 0.1 mM of lead containing 0.6 M KCl. in 0.1 M acetate buffer at pH 4.8 were recorded at various scan rates using only PGE. The recorded cyclic voltammograms figure 7A, showed cathodic reduction peak in the initial (-ve) scan resulting from the reduction of Pb (II) to Pb (0). And the anodic peak achieved on the return on the (+ve) scan showed that Pb had been deposited as PGE [12]. This cyclic voltammograms demonstrate that the quasi-reversible processes (a large peak-to-peak separation), the peak current increase with the scan rate but is not linear in a range from 10 to 100 mV/s figure 7B, the current due to quasi-reversible processes is controlled by both mass transport and charge transfer kinetics [30,31]. whereas the ratio  $I_{pc}/I_{pa}$  is almost constant and has a value around 1.4 indicating a quasi-reversible behavior of lead (II) ions on

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the PGE, With the increase of the scan rate both the anodic ( $I_{pa}$ ) and cathodic ( $I_{pc}$ ) peak currents increased with the scan rate suggesting that lead (II) ions participate in diffusion controlled electrode processes. In figure 7C the  $\log I_p$  Vs  $\log v$  plot present slopes with values close to 0.5 confirming also the diffusion controlled nature of the lead (II) ions electrochemical reactions on the PGE [32]. And 100 mV/s was used for sensitivity in the measurements

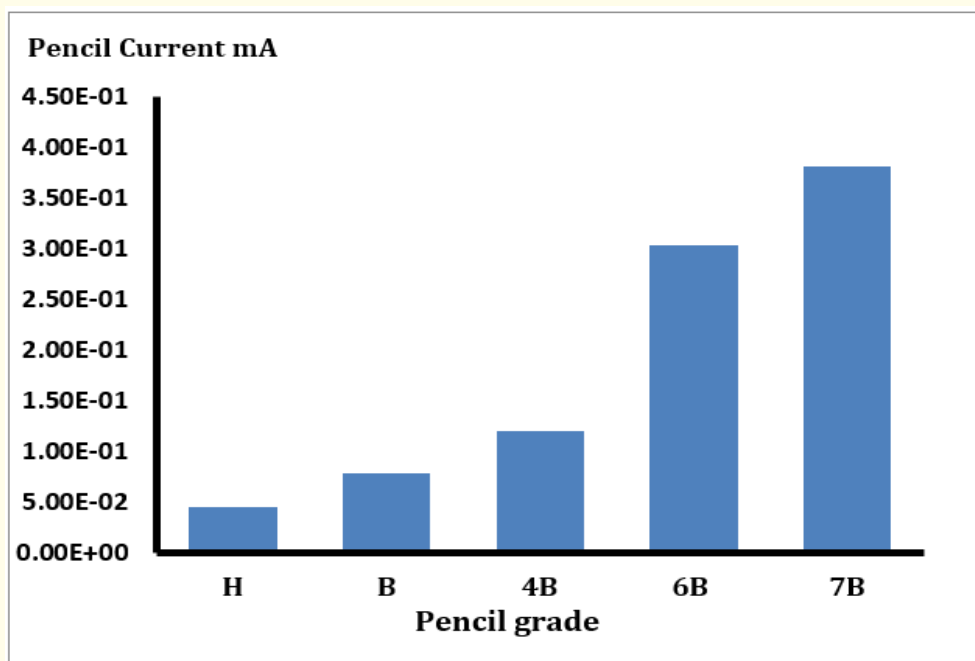
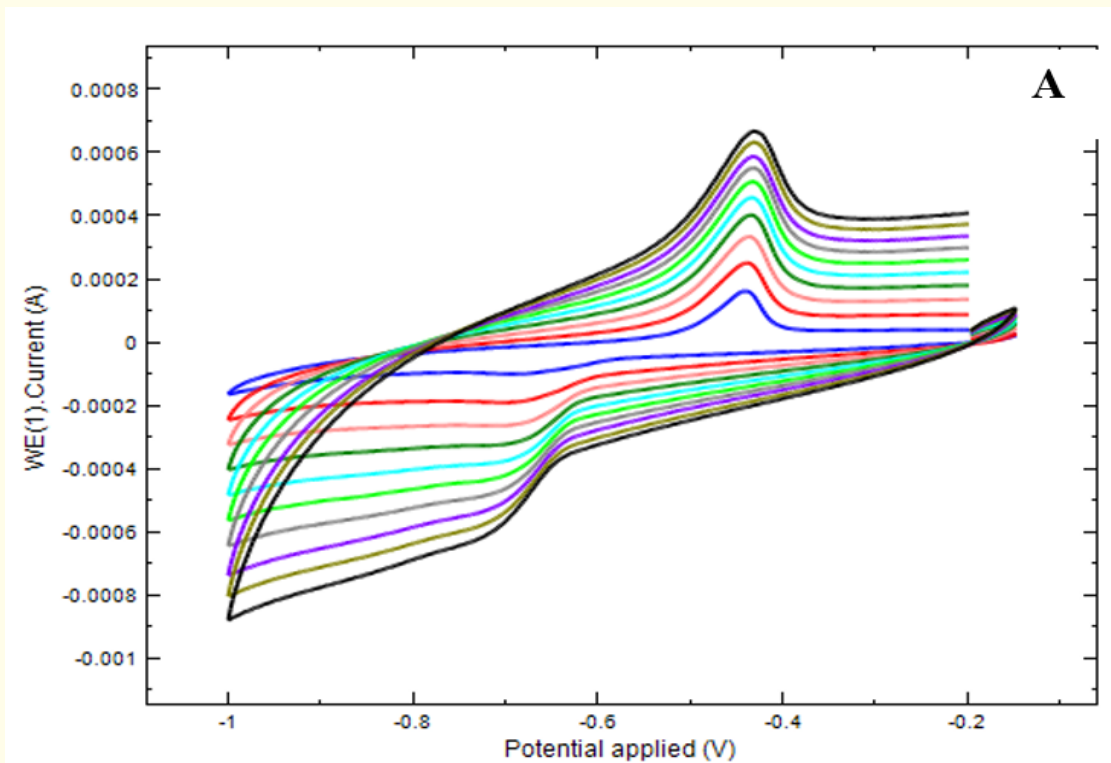


Figure 6: Plot of peak current values versus different graphite grade 0.1 mM Pb, and 0.6 M KCl. in 0.1M acetate buffer at pH (4.8).





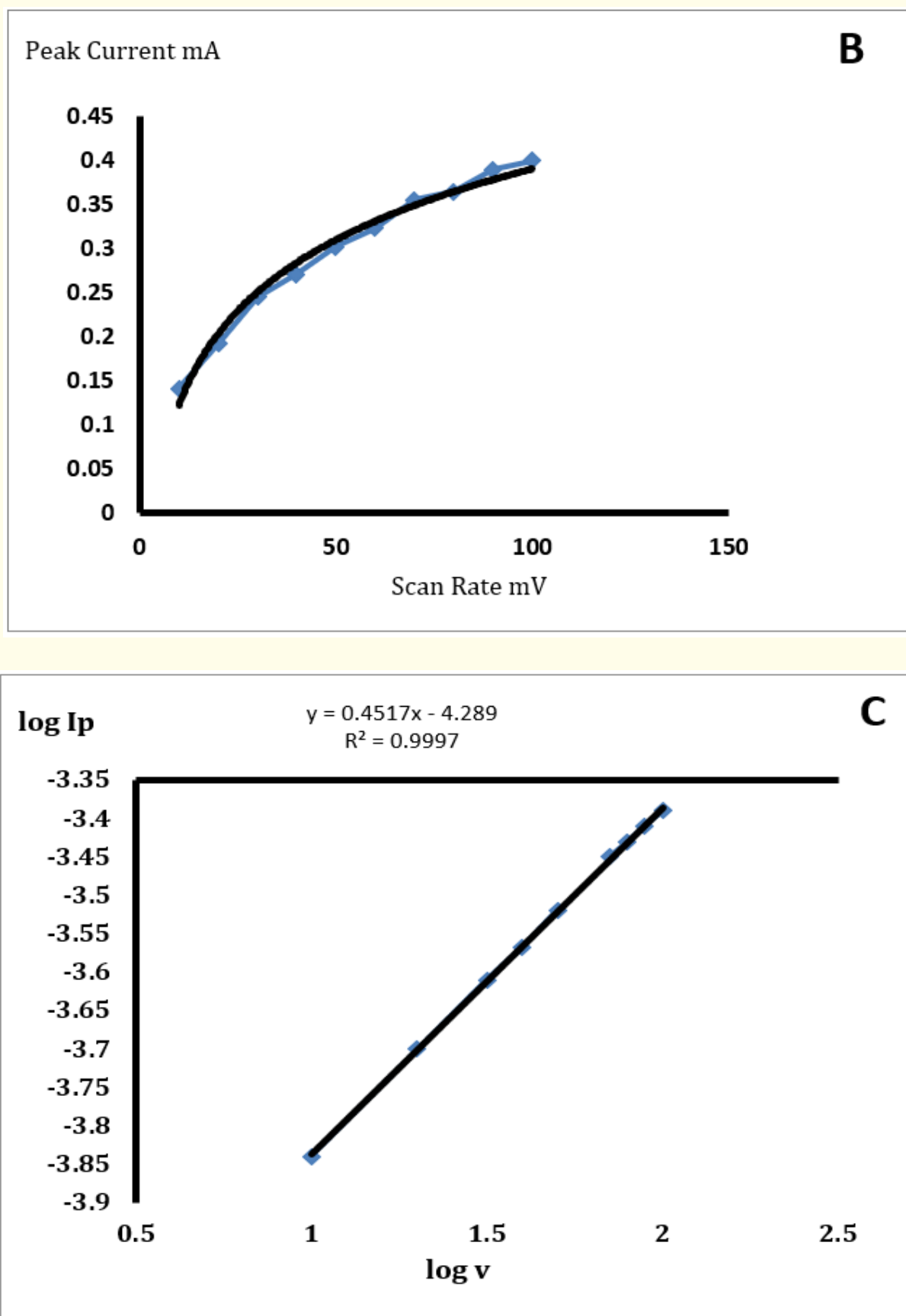
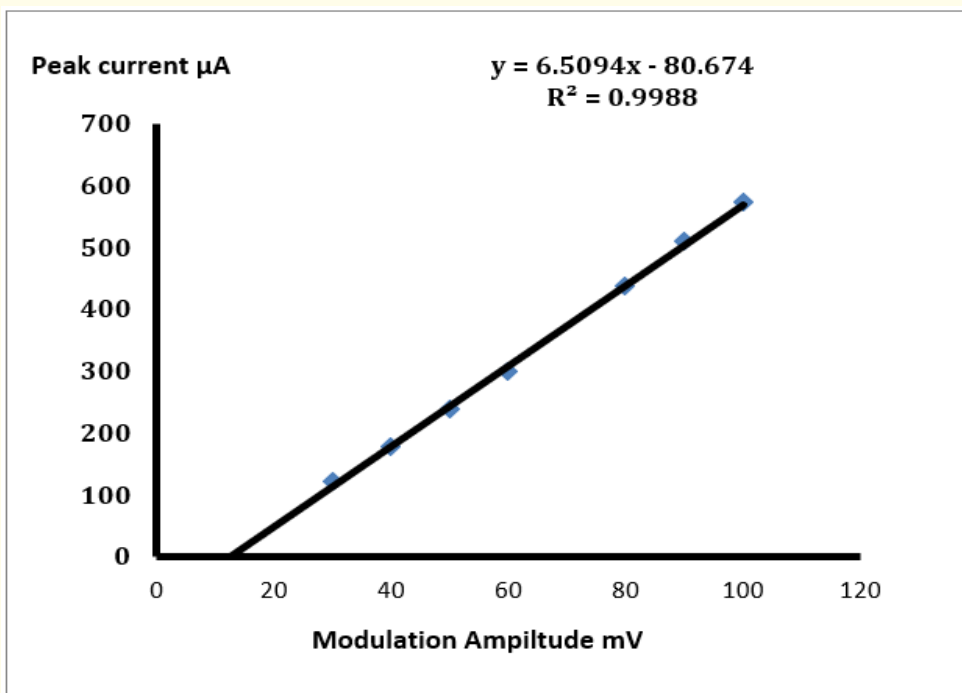


Figure 7: (A) Cyclic Voltammograms of 0.1 mM of lead in PGE at versus scan rate (B) plot of peak area of lead versus scan rate. And (C) A plot of log Ip vs. log v.

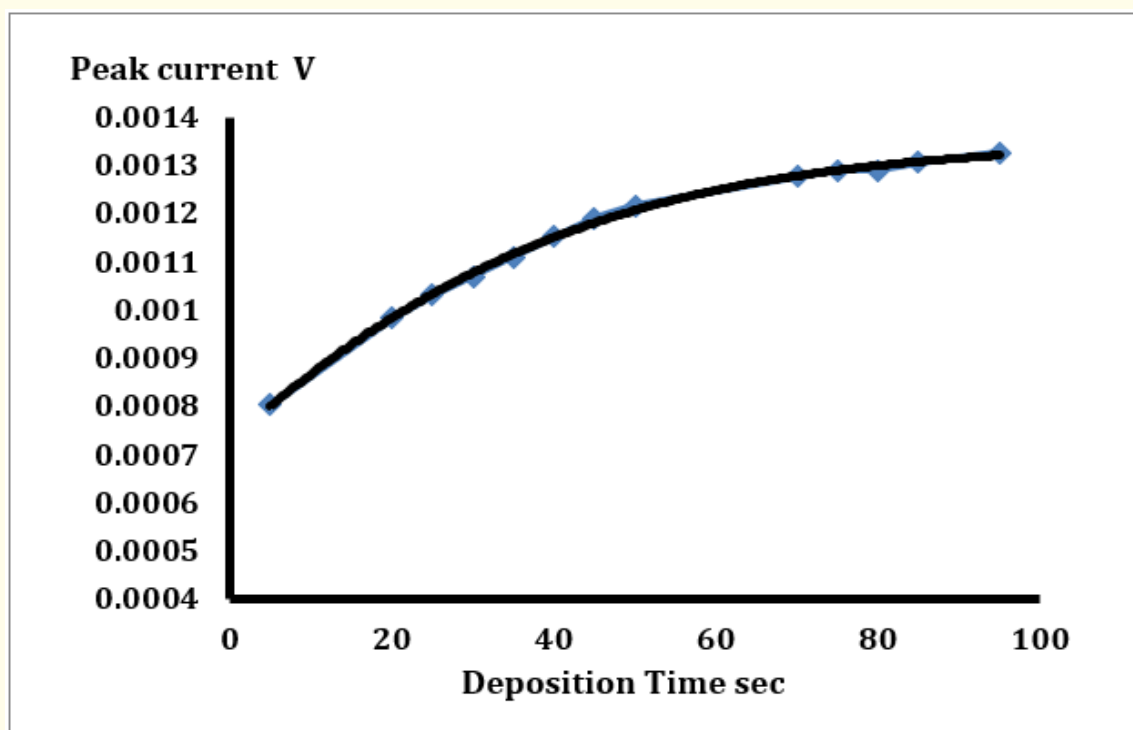
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On the other hand, the peak current increased up to 100 mV when the modulation amplitude was increased. Accordingly, 100 mV was employed for pulse amplitude as shown in figure 8.



**Figure 8:** The effect of Modulation amplitude on the peak height in acetate buffer. Conditions: 0.1 mM Pb, and 0.6 M KCl.

Deposition time is defined as the period of time needed to reduce Pb (II) ions back to its metallic state; the reduction takes place at the electrode while it is immersed in the solution, figure 9 Showed the dependence of peak current on deposition time of Pb (II) [28].

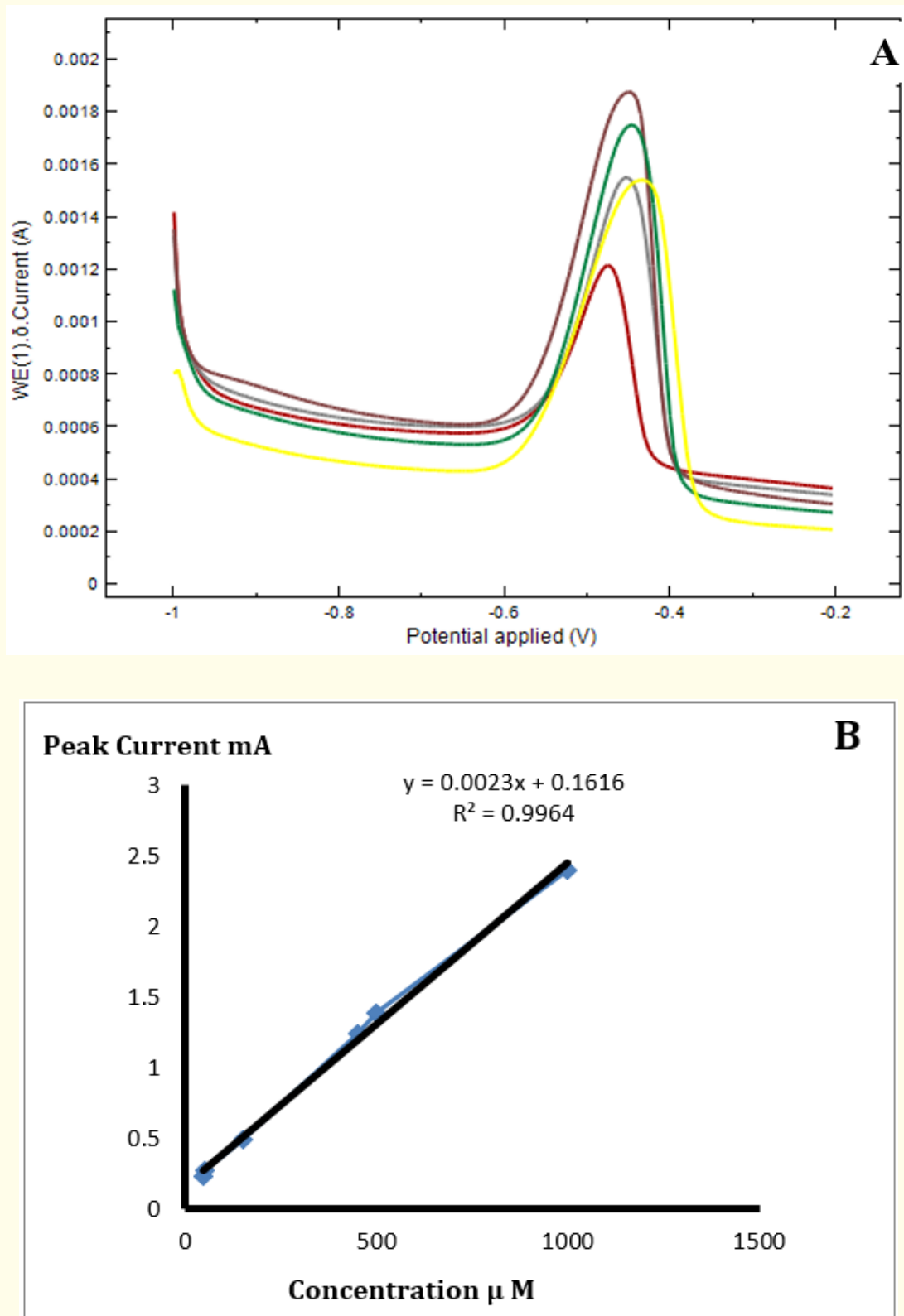


**Figure 9:** The effect of deposition time on the peak current response of a solution containing 0.1 mM Pb, and 0.6M KCl.

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**Calibration curve studies by differential pulse anodic stripping voltammetry**

A calibration curve was performed on standard Pb (II) solutions over the concentration c range 43 - 1000  $\mu\text{M}$  is shown in figure 10, using the optimized conditions as shown above.



**Figure 10:** (A) Some voltammograms and calibration curves obtained for various lead (II) concentrations. (B) Calibration plot for Pb (II) obtained by DPASV; acetate buffer 0.1M, supporting electrolyte 0.6M KCl.

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### Interference study

The interference effects of some heavy metals salts  $Zn^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Cr^{6+}$ ,  $Mn^{6+}$  and  $Cu^{2+}$  ions in addition to diluted acids and bases on the determinations of lead were investigated under the optimum conditions by recording differential pulse voltammograms using 0.10 mM lead and in the presence of approximately 0.10 mM investigated ion. The results showed that those salts and the diluted acid and base did not significantly affect to the peak current.

### Analytical Application

The PGE was evaluated by carrying out Pb (II) determinations on ground water samples obtained from the south Khartoum state, bottled water from the local companies and from the mining areas in eastern Sudan using the optimized conditions as shown above. The data obtained demonstrate that the proposed method has promise for the determination of Pb (II) in such water samples.

### Statistical data

The analytical methods were validated with respect to linearity, Limit of Detection (LOD), Limit of Quantification (LOQ) and precision according to ICH [33,34]. The proposed method was compared statistically with the ICP-OES using T test and F test [35].

### Validation and Analytical application of the method

Under the selected optimum conditions, voltammograms were recorded for the construction of the calibration curve as shown figure 9, the linear relationship was obtained between in concentration range 0.1  $\mu\text{M}$  and 1.0 mM Lead (II). The regression data are presented in table 1. The limit of detection (3s) and the limit of quantification (10s) calculated from the standard deviation of blank data (n = 6).

Parameters	Value
Slope (mA/ $\mu\text{M}$ )	0.0023
Intercept (mA)	0.1616
Standard deviation of slope (mA/ $\mu\text{M}$ )	6.85729E-5
Standard deviation of intercept (mA)	0.03405
Standard deviation of the estimate	0.01272
RSD	1.272%
Linear Correlation coefficient ( $R^2$ )	0.9964
Linear range	45 $\mu\text{M}$ - 1000 $\mu\text{M}$
LOD, $\mu\text{M}$	43.0 $\mu\text{M}$
LOQ, $\mu\text{M}$	130 $\mu\text{M}$
*PDL, $\mu\text{M}$	5.0 $\mu\text{M}$
*PDL= Practical Detection Limit	

**Table 1:** Regression data of the calibration curve.

### Accuracy and Precision of the PGE method

The accuracy and precision of the proposed method were determined at three concentration levels of lead (II) by applying three replicate samples of each concentration. As shown in table 2 indicating high reproducibility of the results and precision of the method. This good level of precision was suitable for determination of lead (II) in environmental samples.

**Robustness of the PGE method:** Robustness was examined by evaluating the influence of small variation in the method variables on its analytical performance. In these experiments, one parameter was varied, whereas the others were kept constant and the recovery percentage was measured. It was found that small change in the variables did not significantly affect the procedures, the recovery values were shown in table 3.

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Concentration $\mu\text{M}$	Found $\mu\text{M}$	Recovery % $\pm$ RSD*
450	475.7	99.2 $\pm$ 1.14
500	538.5	98.8 $\pm$ 1.32
1000	967.3	95.6 $\pm$ 3
*values are mean of three determinations		

**Table 2:** Precision of the PGE method for lead determination.

Parameter		Recovery% $\pm$ RSD*
Standard conditions		
pH	4.7	94.44 $\pm$ 5.09
	4.9	92 $\pm$ 1.81
Volumes of buffer ml	0.5	90 $\pm$ 4.0
	1.5	98.7 $\pm$ 2.24
Scan rate mV	95	102 $\pm$ 2.23
	105	110 $\pm$ 0.79
Pulse amplitude mA	90	100.5 $\pm$ 0.88
	110	107.6 $\pm$ 1.76
Accumulation time sec	80	108.2 $\pm$ 0.82
	100	92.3 $\pm$ 2.4
* values are mean of 3 determinations		

**Table 3:** Robustness of differential pulse anodic stripping voltammetry using pencil graphite electrode PGE for lead(II) determination.

The method was successfully applied for the determination of lead (II) in drinking water samples utilizing the standard addition method. There was no information regarding the lead (II) content in the water sample. Therefore, the accuracy of the method was confirmed by comparing the results with those obtained using ICP-OES as well as by the employing of the recovery test. The results are presented in table 4.

NO	Sample	Proposed method	ICP-OES method
		Lead (II) found $\mu\text{M}$	Lead (II) found $\mu\text{M}$
1.	South Khartoum El- Farouk" city	0.01181	0.0127
2.	Anhar Company	0.00886	0.00965
3.	Alwabil Company	0.00844	0.00805
4.	Gedaref State (Alssabagh locality)	0.0105	0.011
5.	Gedaref State (Wdboshara locality)	0.01899	0.0199

**Table 4:** The results achieved by the proposed method (Differential pulse /anodic stripping voltammetry using Pencil graphite electrode PGE (7B) and ICP-OES methods for the determination of lead (II) ions in water samples.

The concentration of lead (II) ions of each sample that obtained by the proposed method DPASV using PGE was statistically compared with the validated method ICP-OES using T and F test table 5, within confidence level 95%, by conventional criteria, the difference between the two methods is considered to be not statistically significant, this indicated approximately similar accuracy and precision [35].

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Water sample	DPASV	ICP-OES	T-calculated	F-calculated
	Conc $\mu\text{M} \pm \text{RSD}^*$	Conc $\mu\text{M} \pm \text{RSD}^*$		
South Khartoum El Farouk" city	0.01181 $\pm$ 4%	0.0127 $\pm$ 0.78%	0.9649	14.289
Anhar Company	0.00886 $\pm$ 3.9%	0.00965 $\pm$ 0.51%	2.1259	18.447
Alwabil Company	0.00844 $\pm$ 1.85%	0.00805 $\pm$ 0.13%	2.0744	19.444
Gedaref State (Alssabagh locality)	0.0105 $\pm$ 1.90%	0.011 $\pm$ 1.36%	2.2942	1.7143
Gedaref State (Wdboshara locality)	0.01899 $\pm$ 2.6%	0.0199 $\pm$ 1.01%	2.7327	11.149
The value from statistic table			2.78	19.0
*values are mean of three determinations				

**Table 5:** Statistical comparison between the concentration of lead (II) in water samples obtained using the proposed method (DPASV) and the ICP-OES method and T and F value.

**Conclusion**

An easy, inexpensive and rapid differential pulse voltammetry using a disposable pencil graphite electrode PGE was developed and proposed for the determination of lead (II) in drinking water samples. The utilization of disposable pencil graphite electrode provide important advantages over the previously reported methods, the pencil graphite electrode is a good alternative to toxic mercury electrodes, and the other expensive carbon-based electrodes requiring time-consuming preparation and cleaning steps. However, the whole measurement for a sample in the proposed method completed using several PGE lead without electrochemical and mechanical cleaning steps. The results obtained using the proposed method indicate that the method is simple, rapid, selective, and accurate for determination of lead. The method can sufficient be used for monitoring lead content in water according to the WHO guideline.

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