International Journal of Sciences:
Basic and Applied Research
(IJSBAR)

ISSN 2307-4531
(Print & Online)

http://gssrr.org/index.php?journal=JournalOfBasicAndApplied

Simultaneous Determination of Trace Lead (II), Cadmium (II) and Cobalt (II) by Differential Pulse Anodic Stripping Voltammetry Using Polyacrylic acid/Glassy Carbon Electrode

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Abstract

Polyacrylic acid/Glassy carbon electrode (PAA/GCE) was employed for the determination of lead(II), cadmium(II) and cobalt(II). With differential pulse anodic stripping voltammetry, the following optimal conditions were determined: Deposition potential: -0.8V, Accumulation time: 300seconds, amplitude: 0.06V, pulse period: 0.02seconds, pulse width: 0.01seconds and sampling width: 0.0033seconds and pH 6.0. Under these optimal conditions, linear calibration curves were obtained in a range of 125 – 7.8μM for Pb^{2+}, 16 – 2μM for Cd^{2+}, and 2 – 0.125mM for Co^{2+} with detection limits of 0.9nM, 1.9nM and 11.0μM for Pb^{2+}, Cd^{2+} and Co^{2+}, respectively. This film electrode (PAA/GCE) was successfully applied to the determination of Pb(II), Cd(II) and Co(II) in tap water sample.

Keywords: Polyacrylic acid; Glassy carbon electrode; Lead; Cadmium; Cobalt and differential pulse anodic stripping voltammetry.

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1. Introduction

Contamination of water by trace toxic and heavy metals represents a major current environmental problem, which results in an ever-increasing demand for the detection and determination of metal contaminants [1]. Differential pulse anodic stripping voltammetry (DPASV) is a widely used analytical technique for detection of trace heavy metals at low cost. DPASV is based on a preconcentration by electrodeposition of metallic ions from a sample solution onto a working electrode surface, followed by anodic stripping of the analyte from the electrode surface into the sample solution [2, 3]. Recently, polymer-film electrodes have become an attractive new subject of electroanalytical investigations as they could be a potential replacement for mercury and mercury film electrodes. Several types of polymer electrodes have shown excellent advantages over mercury film electrodes when applied to detect trace heavy metals using stripping voltammetry [4, 5].

Several trace metals create environmental and human health concerns when elevated concentrations of these metals are present in the environment. In this regard, cadmium (Cd) and cobalt (Co) are trace metals of prime environmental concern, since they are significant for environmental surveillance, food control, occupational medicine, toxicology and hygiene [6]. Lead (Pb) is another metal that is constantly monitored in natural and drinking water due to the harmful effects that are often manifested in young children [7]. It is also known that several trace metals are regarded as essential micro-nutrients and play an integral role in the life processes of living organisms. In contrast, metals such as lead and cadmium play no biological role in living organisms and lead to toxicity when present [8-10].

Limited success has been achieved with the simultaneous detection of three or more trace metal ions at a transducer surface. The simultaneous analysis of metal ions is typically performed with inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), or atomic absorption spectrometry (AAS). These are well established methods that are characterized by low detection limits, but these methods require expensive instrumentation and trained personnel and cannot be used for field and on-site measurements. On the other hand, anodic stripping voltammetry (ASV) is one of the most favorable techniques for the determination of heavy metal ions due to its low cost, high sensitivity, easy operation and the ability of analysing element speciation [11].

The most sensitive electroanalytical technique, stripping analysis, is highly suitable for the task of field monitoring of toxic metals. The remarkable sensitivity of stripping analysis is attributed to its preconcentration step, in which trace metals are accumulated onto the working electrode. This step is followed by the stripping (measurement) step, in which the metals are "stripped" away from the electrode during an appropriate potential scan. About 30 metals can thus be determined by using electrolytic (reductive) deposition or adsorptive accumulation of a suitable complex onto the electrode surface. Stripping electrodes thus represent a unique type of chemical sensors, where the recognition (accumulation) and transduction (stripping) processes are temporally resolved. Short accumulation times (of 3-5 min) are thus sufficient for convenient quantitation down to the sub-ppb level, with shorter periods (1-2 min) allowing measurements of ppb and sub-ppb concentrations. The time consuming de-aeration step has been eliminated by using modern stripping modes (e.g. potentiometric or square-wave stripping or differential pulse stripping), that are not prone to oxygen interferences. Stripping analysis can provide useful information on the total metal content, as well as characterization of its chemical form (e.g. oxidation state, labile fraction, etc.) [10-13].

Polyacrylic acid (PAA) is a three-dimensional cross-linked polymer network that swells by absorbing water up to hundreds of times its own weight, hence called a superabsorbent [14]. PAA has a variety of applications including drug delivery devices [15], biomaterial for tissue engineering [16], in agriculture [17], and waste water treatment [18], based on its ability to absorb water and to adsorb and retain dissolved substances, such as dyes [19] and heavy metal ions that have environmental impact [20]. In this paper, the use of polyacrylic acid modified GCE as an alternative transducer for the voltammetric stripping and analysis of Pb^{2+}, Cd^{2+} and Co^{2+} ions in aqueous solutions is reported. The experimental parameters such as the deposition time, pH, deposition potential, accumulation time, amplitude, pulse period, pulse width and sampling width were optimized. The modified electrode exhibited attractive stripping performance for trace analysis of Pb(II), Cd(II) and Co(II) compared with plain glassy carbon electrode. Polyacrylic acid modified glassy carbon electrode (PAA/GCE) was also successfully applied to the analysis of Pb(II), Cd(II) and Co(II) in tap water sample.

2. Materials and Methods

2.1 Chemicals and Solutions

Poly(acrylic acid), 25wt% solution in water, Cobalt(II) chloride (AR), cadmium nitrate (AR), lead nitrate (AR), acetic acid glacial (AR) and sodium acetate anhydrous (AR) were from fisher scientific and were used as received. For voltammetry, the electrolyte was acetate buffer. Water was purified to specific resistivity >15 MΩ cm. All other chemicals were reagent grade.

2.2 Apparatus

All the electrochemical experiments were performed with a CHI 1232B Electrochemical Station (CH Instrument Co., USA). A three-electrode system (CH Instrument Co., USA) consisted of a modified glassy carbon working electrode with diameter of 3 mm, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. A pH meter Bench – Model CyberScan pH Tutor (Eutech Instruments) was used for all pH measurement. All experiments were carried out in a 10.0mL electrochemical cell at $23 \pm 0.2\ ^{o}C$.

2.3 Film Preparation

Glassy carbon disk electrodes (3 mm diameter) were abraded on wet silicon carbide paper (400 grit, Buehler) followed by (600 grit, Buehler). Rinsed in water, then polished thoroughly with 0.05 micron micropolish (CH Instruments) slurry on a soft cloth before sonicated in ethanol and distilled water for 3 min each to remove particles and other possible contaminants. The actual surface area determined by cyclic voltammetry using ferrocyanide oxidation was $0.071 cm^2$. 10μl freshly prepared 4mM polyacrylic acid were deposited on the polished electrode and allowed to react at room temperature for 20 minutes. After 20 minutes, the electrodes were rinsed with de-ionized water before use.

2.4 Procedure

All measurements were carried out in the differential pulse anodic stripping voltammetric (DPASV) mode. The differential pulse stripping voltammograms were recorded from 0V to -1.45V followed by a 10 s rest period. Prior to the next determination, the modified electrode was activated for 60 s in a pH 6.0 acetate buffer to remove the previous deposits completely.

Tap water sample was collected from our research laboratory (Nairobi city, Kenya) for the determination of Pb(II), Cd(II) and Co(II). 3mL of this water sample and 3mL of acetate buffer (pH 6) were put into voltammetric cell. After the solution was de-aerated by purging with nitrogen, Pb, Cd and Co heavy metals were analyzed at the following condition: Deposition potential: -0.8V, Accumulation time: 300seconds, amplitude: 0.06V, pulse period: 0.02seconds, pulse width: 0.01seconds and sampling width: 0.0033seconds. After a rest period of 10sec, the potential scan was started in the anodic direction using the differential pulse mode. After the addition of 100µl of the mixture standard solution, the procedure was repeated three times. Voltammetric current readings were taken and used for quantitative analysis.

3. Results and Discussions

3.1 Optimization

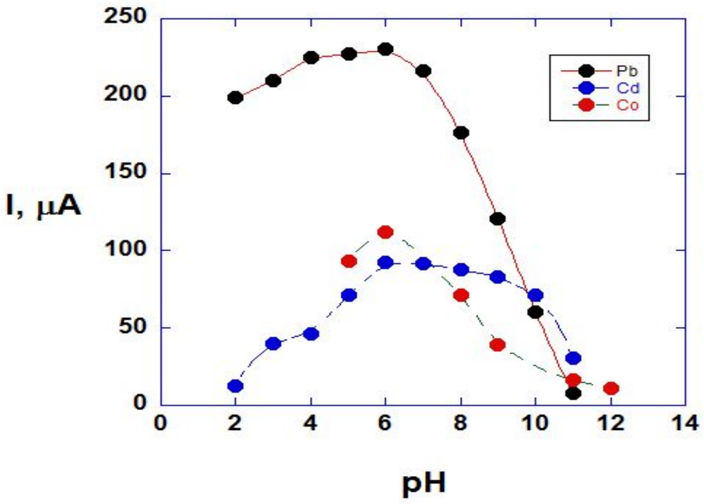

Figure 1: Effects of pH on the peak currents of 2mM Pb(II), 2mM Cd(II) and 2mM Co(II) at the PAA/GCE in acetate buffer of pH 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 values.

The electrochemical responses of 2mM Pb(II), Cd(II) and Co(II) in acetate buffer with different pH values at the PAA/GCE were studied by DPASV, and the results are shown in Figure 1. It can be seen from Figure 1 that the maximum peak current responses for both Pb(II), Cd(II) and Co(II) were obtained when pH was 6.0. When the pH value increased to 7.0 and above the peak current began to gradually decrease. Consequently, a pH 6.0 acetate buffer was selected for further work.

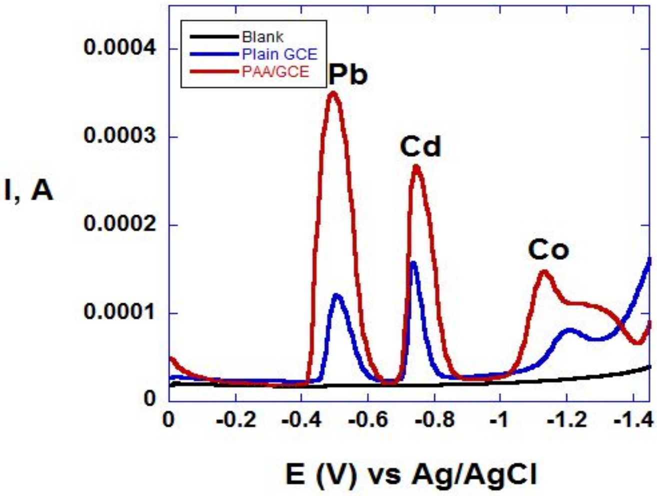

Figure 2: Differential Pulse Anodic Stripping Voltammograms of 2mM Pb(II), Cd(II) and Co(II) at pH 6 on Plain GCE (***Blue***) and PAA/GCE (***Red***).

Figure 2 shows the differential pulse anodic stripping voltammetric responses of Pb(II), Cd(II) and Co(II) at the GCE plain and PAA/GCE at pH 6.0. The response signals on the bare GCE are at potentials -0.495V for Pb(II), -0.720V for Cd(II) and -1.215V for Co(II) while for PAA/GCE are -0.480V for Pb(II), -0.745V for Cd(II) and -1.190V for Co(II). The peak potential maxima results obtained have shown that the peaks for the different metal ions can be identified as Pb(II), Cd(II) and Co(II). With PAA/GCE, the stripping current peaks for Pb(II), Cd(II) and Co(II) are remarkably higher compared to plain GCE under similar conditions. This further indicate that the PAA/GCE sensor can greatly promote the pre-concentration of Pb^{2+}, Cd^{2+} and Co^{2+} ions at the electrode and significantly increase the sensitivity for the determination of Pb^{2+}, Cd^{2+} and Co^{2+} ions. This indicates that PAA possibly increases the adsorption of metal ions onto the electrode surface. Similar behavior was observed previously by Elamathi, S. et al [21] and Magdy, Y. et al [22].

The effects of the deposition time on the stripping peak currents of Pb(II), Cd(II) and Co(II) were studied from 0 minutes to 10 minutes and the results are shown in Figure 3. It can be seen from Figure 3 that the peak currents increased linearly from 0 minutes up to 5 minutes. As improving the deposition time, more and more metals accumulated at the surface of modified electrode, so the peak currents greatly increased. However, when the deposition time was beyond 5 minutes, the peak currents started to level off, indicating that the amount of metals at the electrode surface tends to saturation. In view both of sensitivity and deposition time in this work, 5 minutes was selected as the deposition time.

Figure 4 shows differential pulse anodic stripping voltammograms obtained when the amplitude, sampling width, pulse period and pulse width were varied. The best optimal conditions which provide the highest response currents and well defined peaks are summarized in table 1.

3.2: Calibration

Figure 5 shows the DPASVs measured from the PAA/GCEs for the detection of Pb^{2+}, Cd^{2+} and Co^{2+} with the concentrations varying from 2mM to 0.9nM each in the acetate buffer, pH 6.0 for 300 seconds deposition time. The calibration curves for the Pb^{2+}, Cd^{2+} and Co^{2+} are linear in the range of 125 – 7.8µM for Pb^{2+}, 16 – 2µM for Cd^{2+}, and 2 – 0.125mM for Co^{2+} (Figure 4). The detection limits of Pb^{2+}, Cd^{2+} and Co^{2+} were found to be about 0.9nM, 1.9nM and 11.0µM, respectively.

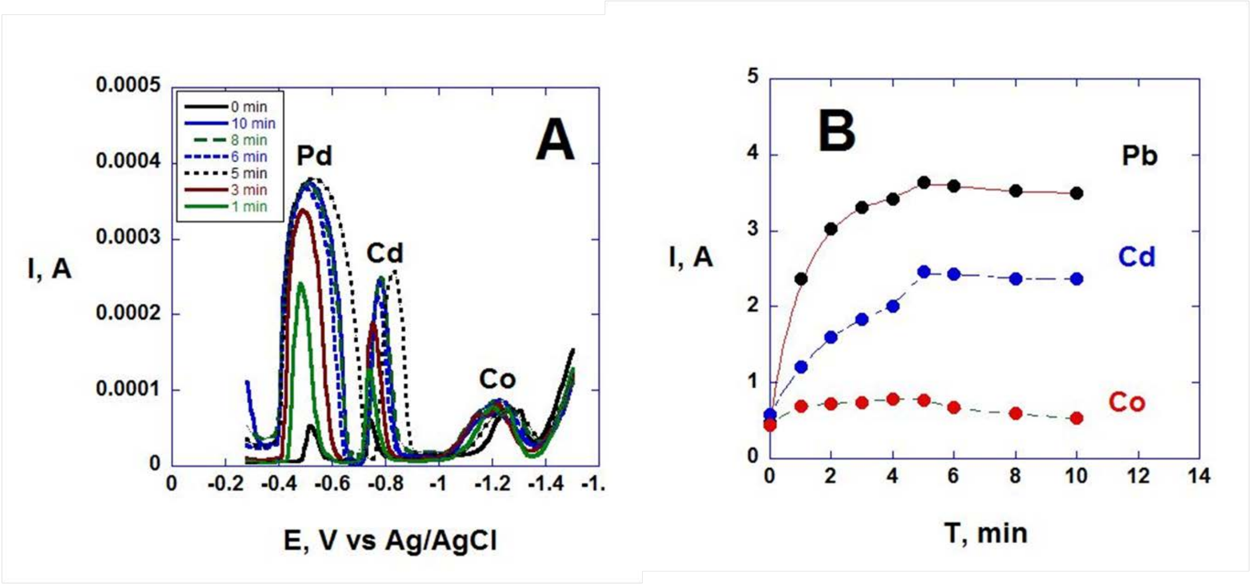

Figure 3: Effect of the deposition time on the peak currents of Pb, Cd and Co in acetate buffer, pH 6.0 containing 2 mM of Pb, Cd and Co at the PAA/GCE. Deposition time: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 minutes. **(A)** DPASVs and **(B)** Current versus Time.

Table 1: Optimal parameters for the simultaneous determination of Pb, Cd and Co on PAA/GCE electrode.

PAA/GCE Electrode	Optimal Parameter Determined
1. Deposition potential	-0.8V
2. Accumulation time	300seconds
3. Amplitude	0.06V
4. Pulse period	0.02seconds
5. Pulse width	0.01seconds
6. Sampling width	0.0033seconds
7. pH	6.0

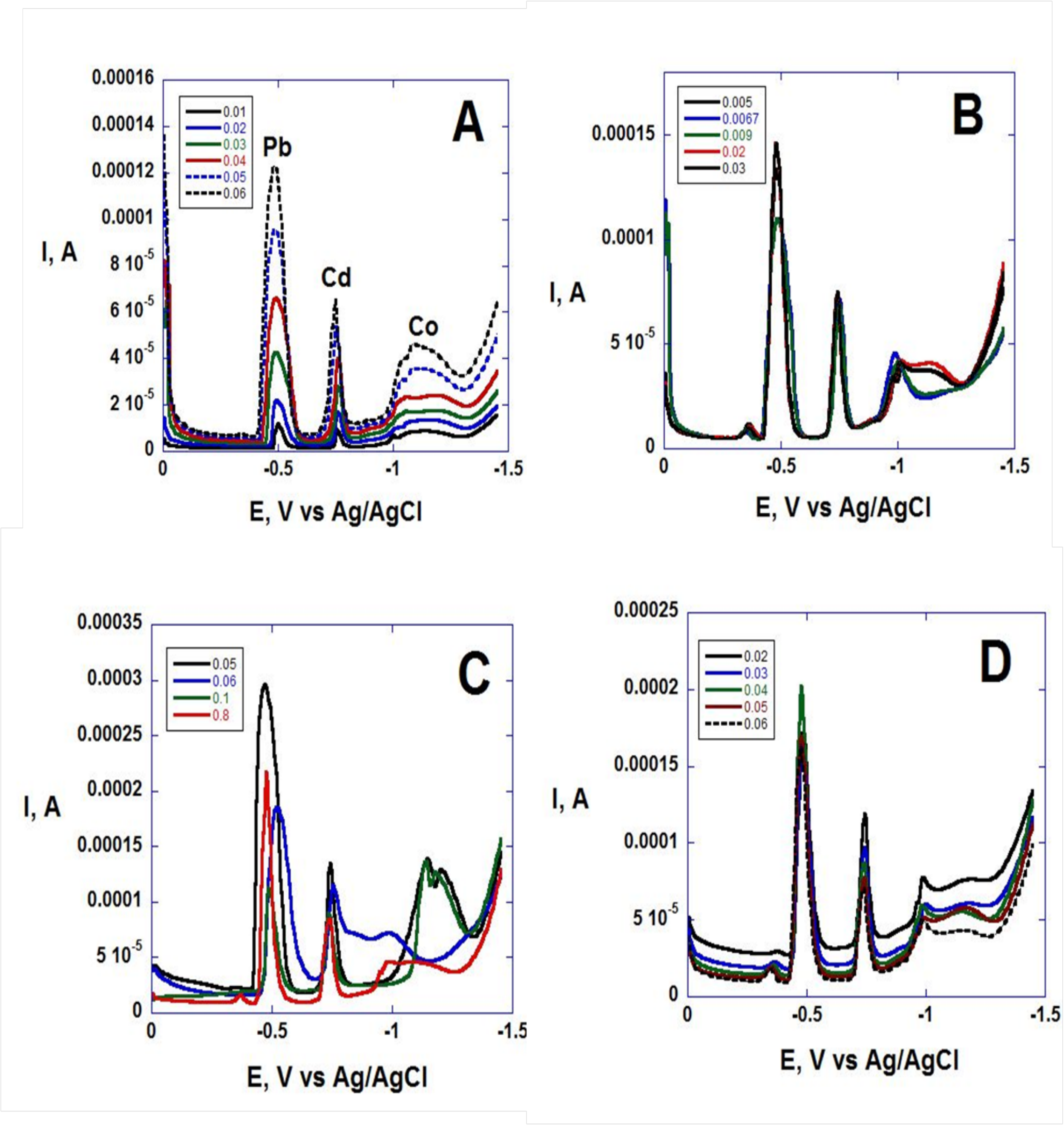

Figure 4: Differential pulse stripping voltammetric responses at the PAA/GCE in buffer pH 6.0 containing 2mM Pb, Cd and Co. **(A)** Amplitudes: 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06V **(B)** Sampling widths: 0.005, 0.0067, 0.009, 0.02 and 0.03 seconds **(C)** Pulse periods: 0.05, 0.06, 0.1 and 0.8 seconds and **(D)** Pulse widths: 0.02, 0.03, 0.04, 0.05 and 0.06 seconds.

3.3: Determination of Pb(II), Cd(II) and Co(II) in Tap Water Sample

As can be seen from the Figure 6, the current peaks of Lead and Cadmium increased by the addition of the standard solution. Under the optimal conditions established above, the concentration of Pb(II), Cd(II) and Co(II) in tap water of Nairobi City was found to be 0.008 mg L^{-1} of Lead(II) and 0.001 mgL^{-1} of Cadmium(II). Cobalt(II) was not detected in the tap water. This value is within the limit values suggested by WHO, EU and

EPA (Table 2). In addition, the concentration of Pb(II) and Cd(II) found indicates to be “the first quality water” of the tap water according to the inland water quality classification [23 - 24].

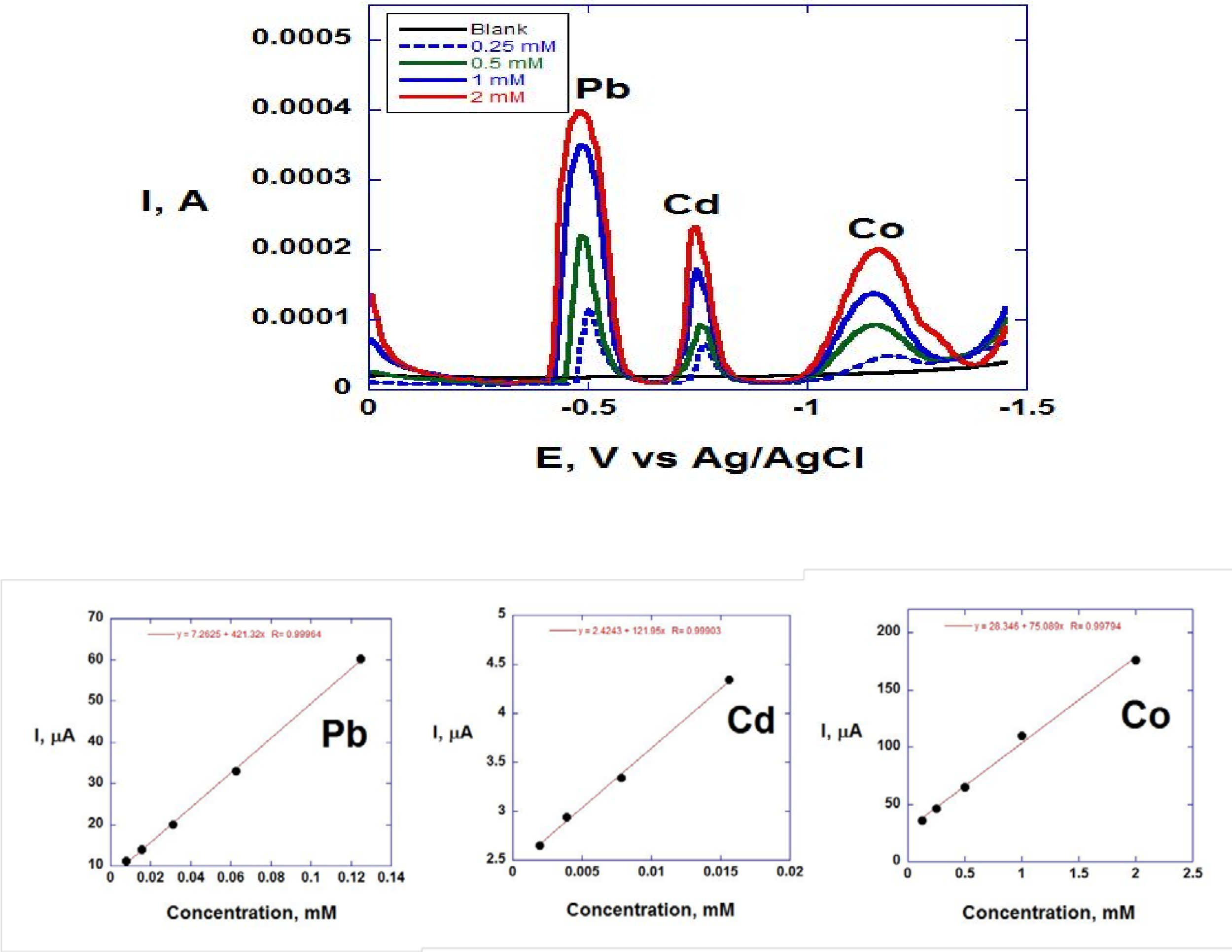

Figure 5: DPASVs of Cd, Co and Pb having concentrations of 2.0, 1.0, 0.5 and 0.125mM from bottom to top, respectively, which were measured using PAA/GCE. Also respective calibration curves for the determination of Cd, Co and Pb of different concentrations are shown.

Table 2: Pb, Cd and Co allowed limit values Limit value (according to EU, WHO and EPA: [23 - 24] and the found value of Lead, Cadmium and Cobalt heavy metals in tap water of Nairobi City (Kenya)

Heavy Metal	**WHO** (mg/L)	**EPA** (mg/L)	**EU** (mg/L)	**Values obtained** (mg/L)
Pb	0.01	0.015	0.01	0.008±0.001
Cd	0.003	0.005	0.005	0.001±0.0002
Co	0.05	-	-	Not found

* ***WHO**: World Health Organization, **EPA:** Environmental Protection Agency, and **EU**: European Union.*

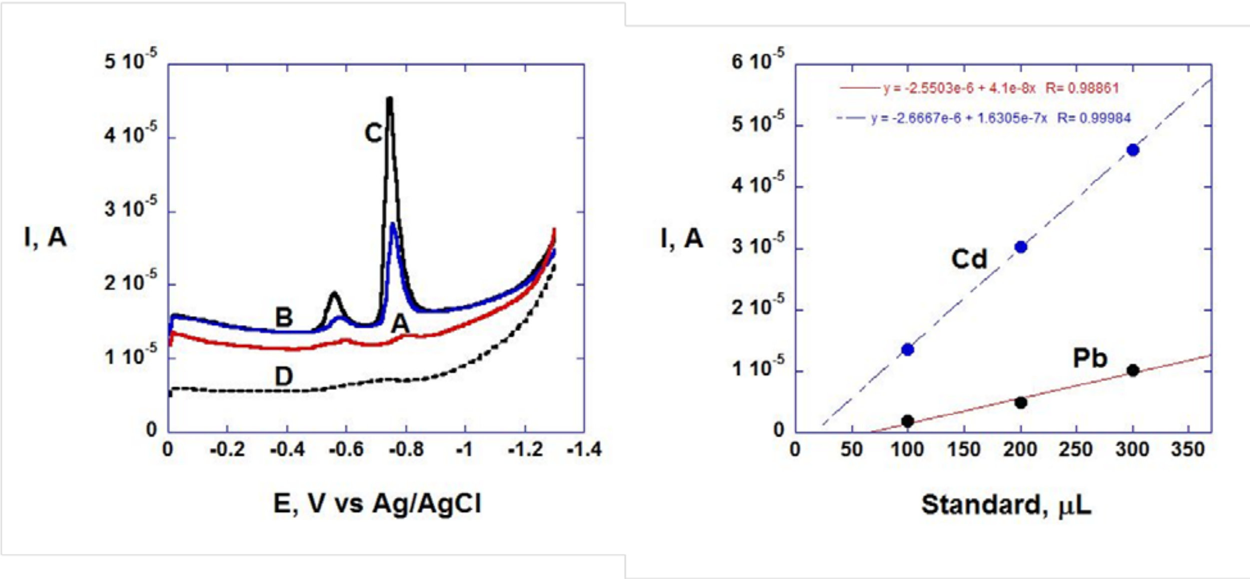

Figure 6: DPAS voltamograms of the Pb, Cd and Co obtained from standard addition technique (**A**) 3ml acetate buffer (pH = 6.0) + 3ml tap water (**B**) A + 100μL of 2mM standard solution of Pb, Cd and Co **(C)** A + 200μL of 2mM standard solution of Pb, Cd and Co. The calibration plots of Pb(II), CdII) and Co(II) were obtained from standard addition by DPASV technique.

4. Conclusion

A simple differential pulse anodic stripping voltammetric sensor based on Polyacrylic acid/Glassy carbon electrode has been developed for the simultaneous determination of lead(II), cadmium(II) and cobalt(II). The optimal conditions were found to be: Deposition potential: -0.8V, Accumulation time: 300seconds, amplitude: 0.06V, pulse period: 0.02seconds, pulse width: 0.01seconds and sampling width: 0.0033seconds. The detection limits of of Pb^{2+}, Cd^{2+} and Co^{2+} were found to be about 0.9nM, 1.9nM and 11.0μM, respectively. This electrochemical sensor successfully determined Pb^{2+}, Cd^{2+} and Co^{2+} ions simultaneously in tap water.

Acknowledgements

This work was supported by the research grants from The Third World Academy of Sciences (TWAS), Italy and Deans' Research Grant (DRG), University of Nairobi.

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