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Electroanalytical determination of heavy metals in drinking waters in the eastern province of Saudi Arabia

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ABSTRACT

The direct and simultaneous determination of lead(II), cadmium(II), and zinc(II) heavy metals in drinking water was carried out using the square wave adsorptive stripping voltammetric (SWASV) technique at different Bi-modified carbon electrode surfaces, including glassy carbon, carbon paste, and graphite pencil. Among the various trace metal technologies, electrochemical stripping analysis is most likely to meet the requirements of on-site metal analysis. In the absence or presence of 600 ppb Bi(III) in an acetate buffer solution (0.1 M, pH 3.5), the metal ions were deposited by reduction at –1.4 V (vs. Ag/AgCl Sat. KCl) onto the carbon electrode surfaces. The deposited metals were oxidized by scanning the potential of the electrode surface from –1.5 to 0.0 V using the SWASV measurements. The stripping currents arising from the oxidation of the corresponding metals were correlated to the concentration of the metals in the water sample. The analytical utility of the bismuth-coated sensors developed here depended on an understanding of their fundamental properties. The obtained results enable heavy metal detection at low (ppb) detection limits, significantly impact the monitoring of inorganic contaminants in drinking water, and improve our management of drinking water supplies.

Keywords: Drinking water; Heavy metals; Zinc(II); Cadmium(II); Lead(II); Square-wave adsorptive stripping voltammetry

1. Introduction

Environmental pollution and human exposure to heavy metals has dramatically increased over the last 50 years due to the increased use of these metals in industrial processes. Knowledge of the heavy metal concentrations in drinking water is essential to understanding the role of these elements in human health [1,2]. Heavy metal contamination of drinking water is a major global problem. Acute lead poisoning in children can cause anorexia, vomiting, malaise, convulsions, and even permanent brain damage. Chronic lead poisoning can cause weight loss, weakness, and anemia. Lead can leach into water from the solder used to join copper pipes, lead pipes in older buildings, lead paint in older buildings, or from dust and soil contaminated with tetraethyl-lead (formerly a gasoline additive) [3]. Cadmium is classified as a priority pollutant by the US Environmental Protection

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Agency due to its broad emission sources and extreme toxicity to human beings, even in low concentrations [4,5]. It is a probable carcinogen and damages the human immune and central nervous systems to cause serious diseases, including renal dysfunction and liver damage [6,7]. A potential source of cadmium contamination in drinking water is industrial wastewater. Industrial sources include the waste from the processes associated with smelting and refining, and the manufacture of pesticides, fertilizers, dyes, pigments, textile operations [8]. Cadmium contamination in drinking water may also arise from impurities in the zinc of galvanized pipes and certain metal fittings [9]. Industrial and household waste discharges, directly or indirectly through leakages in the sewage systems into water sources, excessively pollute surface and ground water [10]. Water quality depends on the physical, chemical, and biological components of water.

Investigations of toxic heavy metals, such as Pb(II), Cd(II), Ni(II), Cu(II), Zn(II), or Cr(III), have gained special importance in food analysis [11], soil, indoor airborne particulate matter [12], and in seawater [13] environmental samples analysis. There is a pressing need to develop an analytical method that traces the elemental analysis of heavy metals in drinking water samples. The direct determination of Zn(II) in tap water samples is enabled by anodic stripping voltammetry techniques [14].

Atomic absorption spectroscopy techniques are used as standard methods for trace metal determination [15–17] due to their sensitivity and low operation costs. Unfortunately, these techniques only detect the presence of one element at a time. Inductively coupled plasma optical emission spectrometry (ICP-OES) can measure several elements at the same time with fairly good detection limits [18], although the technique's operational and maintenance costs stand in the way of the widespread adoption of this technique.

Stripping analysis offers a powerful technique for determining trace metals in environmental, clinical, and industrial samples [19]. Several modifiers have been explored, including mercury [20], gold nanoparticles [21], lead [22], platinum nanoparticles [23], bulk bismuth [24], and bismuth nanoparticles [25], all of which facilitate the precipitation of an amalgam and the formation of electropositive elements. Other studies have suggested the use of dimetallic alloys that enhance detection, including tin–bismuth [26].

The present study involved the screening of a variety of possible transducers to develop an electroanalytical method of simultaneously detecting the targeted heavy metals at low concentration levels. The best transducer among the electrodes was chosen, optimized, and used to test/analyze the drinking water samples collected from the Eastern Province, Saudi Arabia. The obtained results were validated using Inductively coupled plasma-mass spectrometry (ICP-MS) and were compared to the universal standards set by the EPA, EU, and WHO [27,28].

2. Experimental

2.1. Chemicals and instruments

Standard solutions were prepared from 1,000 ppm bismuth, zinc, lead, and cadmium AAS standard solutions obtained from Fluka Analytical. An acetate buffer solution (0.1 M, pH 4.5) was obtained from Sigma (USA).

Voltammetry measurements were performed using an electrochemical workstation (CHI1140A, CH Instruments Inc., Austin, TX, USA). The Ag/AgCl reference electrode (in 3 M KCl, CHI111, CH Instruments Inc.), glassy carbon working electrode (abbreviated GCE, CHI 112, CH Instruments Inc.), and platinum wire counter electrode (CHI115, CH Instruments Inc.) were inserted into a 5.0-mL plastic cell through holes in its Teflon cover.

ICP-MS (Thermo Scientific, USA) was employed to measure the concentrations of Zn(II), Cd(II), and Pb(II) concentrations in drinking water samples.

2.2. Electrochemical transducer preparation

A GCE 3 mm in diameter was polished using 0.3 μm alpha alumina powder, washed with double-distilled water, and tested. A carbon paste electrode (CPE) was prepared by hand-mixing 70 mg graphite carbon powder with 30 mg mineral oil. A small portion of the resulting paste was then packed firmly into a cavity of the PTFE sleeve. Electrical contact was established using a copper wire. The paste surface was smoothed with a weighing paper. A Jedo mechanical pencil (Korea) was used as a holder for both the bare and pretreated graphite pencil leads. Electrical contact with the lead was achieved by soldering copper wire to the metallic part that holds the lead in place inside the pencil. The pencil was fixed vertically such that 15 mm of the pencil lead extended outside of the holder, and 10 mm of the lead was immersed in the solution. This length corresponds to a geometric electrode area of 15.90 mm^2.

2.3. Procedure

Square wave adsorptive stripping voltammetry (SWASV) measurements were performed by applying a +0.6 V potential to the surface for 60 s, followed by 120 s accumulation at –1.4 V in a stirred solution containing 0.1 M acetate buffer (pH 3.5). This step was followed by a subsequent stripping step using a square wave voltammetric waveform with a 6 mV potential step, 80 Hz frequency, and 40 mV amplitude. The GCE surface was polished and the CPE surface was smoothed or renewed, and each electrode was rinsed carefully with deionized water prior to each measurement.

3. Results and discussion

3.1. Transducer selection

We screened different transducers in the presence of Bi(III), as shown in (Fig. 1). The transducers tested were the GCE (Fig. 1(a)), the CPE (Fig. 1(b)), and the

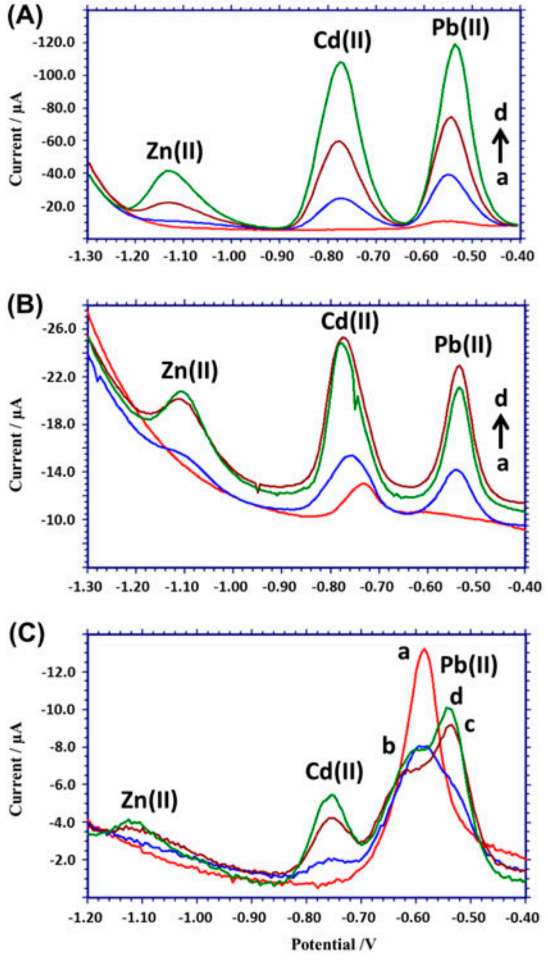

Fig. 1. SWASVs of Zn(II), Cd(II), and Pb(II) in the presence of 600 ppb Bi(III) in acetate buffer solution (0.1 M, pH 3.5) at (A) Glassy carbon, (B) Carbon paste, and (C) Graphite pencil electrodes. Amplitude, 60 mV; Frequency, 100 Hz; Potential increment, 8 mV; Accumulation time, 2.0 min at −1.4 V. For each of Zn(II), Cd(II), and Pb(II) concentrations: (a) 0.0 ppb, (b) 20 ppb, (c) 40 ppb, and (d) 60 ppb.

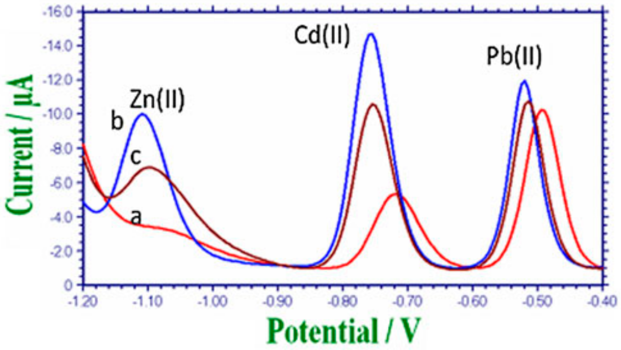

Fig. 2. SWASVs of 40 ppb of each of Zn(II), Cd(II), and Pb(II) at GCE in presence of 600 ppb Bi(III) in acetate buffer solution (0.1 M) at different pH values: (a) pH 3.0, (b) pH 3.5, and (c) pH 4.0. Other conditions as in Fig. 1.

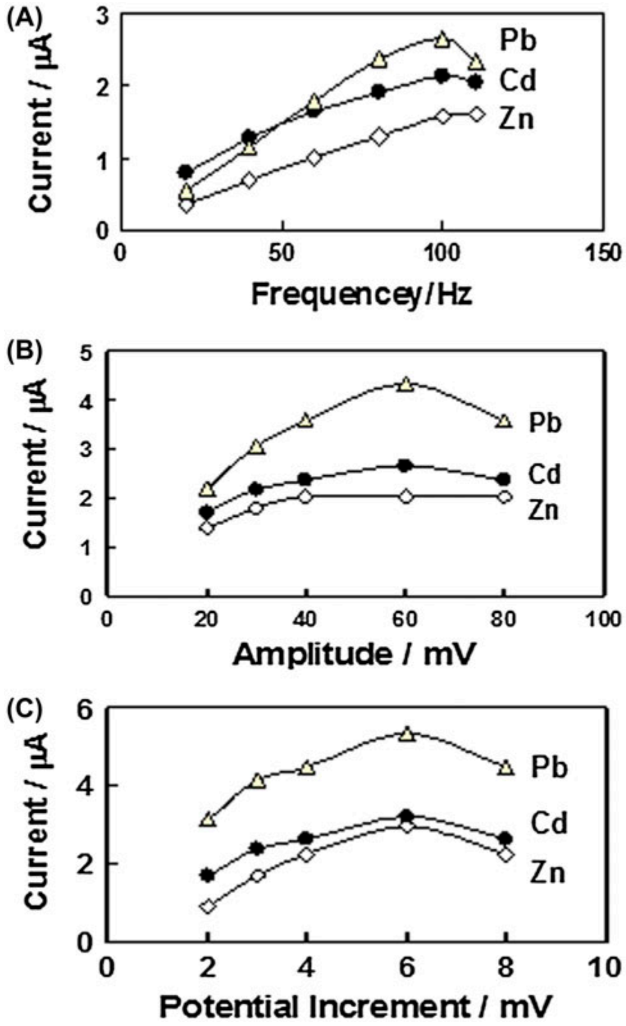

Fig. 3. Effect of (A) Frequency, (B) Pulse Amplitude, and (C) Potential Increments on the SWV responses of 40 ppb Zn(II), Cd(II), and Pb(II) at GCE-Bi-modified surfaces in acetate buffer solution (0.1 M, pH 3.5). Accumulation time, 2.0 min at −1.4 V.

graphite pencil electrode (GPE, Fig. 1(c)). Fig. 1 shows the response obtained from the GCE-Bi at four concentrations: 0.0, 20, 40, and 60 ppb of each of Zn(II), Cd(II), and Pb(II) heavy metal ions. A relatively high background was obtained from the CPE, which is a composite material containing 70% graphite carbon and 30% mineral oil [29]. Because the graphite pencil electrode is a mixture of graphite, wax, and clay [30], the proportions of which impart different properties to the pencil, quite low signal-to-noise ratios were obtained from all metal solutions investigated. As shown clearly in Fig. 1, the GCE was the best transducer among the electrodes tested with respect to the peak shape and sensitivity to all three heavy metals. The GCE, therefore, was used in all subsequent experiments.

3.2. Optimization

Fig. 2(a) shows the SWASV responses measured from the 20 ppb Zn, Cd, and Pb solutions at the glassy carbon electrode (GCE) in acetate buffer solutions at different pH values. A slight cathodic potential shift was observed in the Zn(II), Cd(II), and Pb(II) oxidation peak positions as the pH increased. In the acetate medium, a pH of 4.5 was found to be optimal for maximizing the height and shape of the measured oxidation peak.

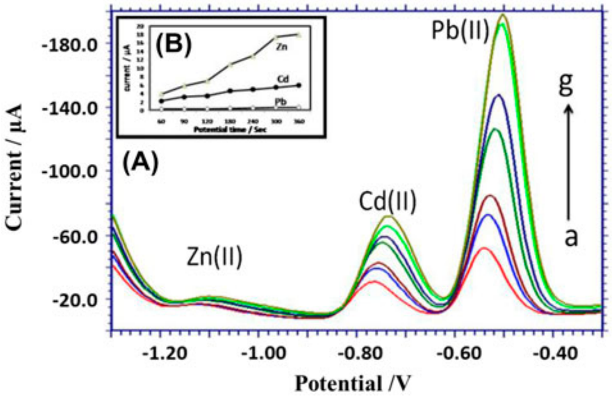

Fig. 4. (A) SWASVs of 40 ppb of each of Zn(II), Cd(II), and Pb(II) at GCE in the presence of 600 ppb Bi(III) in acetate buffer solution (0.1 M, pH 3.5). Amplitude, 60 mV; Frequency, 100 Hz; Potential increment, 8 mV; Accumulation potential −1.4 V for: (a) 60 s, (b) 90 s, (c) 120 s, (d) 180 s, (e) 240 s, (f) 300 s, and (g) 360 s. (B) The corresponding plot.

Fig. 2 shows the SWASV responses of the 40 ppb Zn (II), Cd(II), and Pb(II) solutions at the bismuth-modified GCE (Bi-GCE) in acetate buffer solutions at different pH values. A 50 mV cathodic potential shift was measured in the Zn(II), Cd(II), and Pb(II) oxidation peak positions as the pH increased from 3.0 to 3.5. Fig. 2 shows that the SWASV of Cd(II) increased over the pH range 3.0–3.5 and then decreased. At low pH values (3.0), the decrease in the stripping peak current of Cd (II) could be attributed to an increase in hydrogen generation at the electrode [31]. Nevertheless, at higher pH values, Bi(III) tended to hydrolyze [32] and form

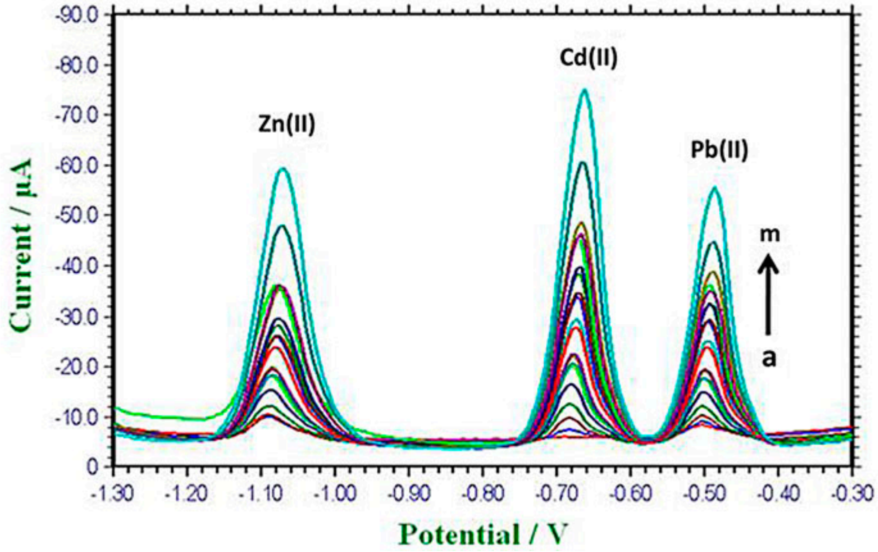

Fig. 5. SWASV of Zn(II), Cd(II), and Pb(II) at GCE-Bi electrode in acetate buffer solution (0.1 M, pH 3.5); Amplitude, 60 mV; Frequency, 100 Hz; Potential increment, 8 mV; Accumulation time, 2.0 min at −1.4 V. Mixture of Zn(II), Cd(II), and Pb(II) concentrations: (a) 0.0, (b) 1.0, (c) 3.0, (d) 5.0, (e) 10.0, (f) 15.0, (g) 20.0, (h) 25.0, (i) 30.0, (j) 35.0, (k) 40.0, (l) 45.0, and (m) 50.0 ppb.

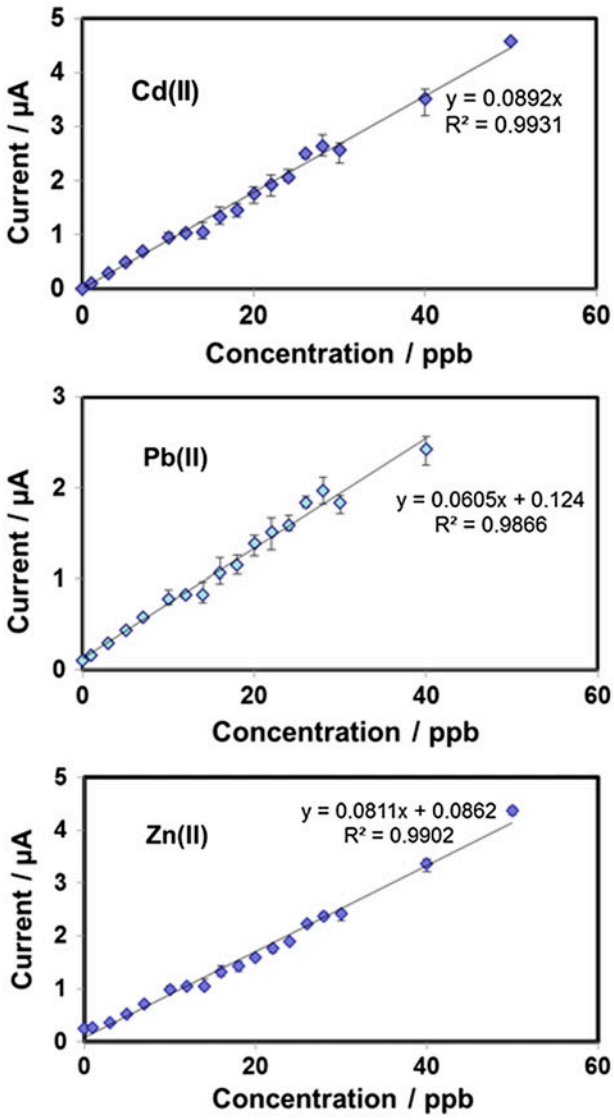

Fig. 6. The corresponding calibration plots. Other conditions are similar to Fig. 5.

deposition compounds that decreased the response to Cd(II). Therefore, an acetate buffer solution having a pH of 3.5 was chosen as the background electrolyte solution in all subsequent experiments.

The SWASV responses obtained from the Zn(II), Cd(II), and Pb(II) solutions were studied at different frequencies over the range 20–110 Hz, as shown in Fig. 3(a). The plots were linear up to 80 Hz, after which they leveled off. A frequency of 80 Hz was chosen as the optimum value. On the other hand, larger pulse amplitudes yielded higher Zn(II), Cd(II), and Pb (II) stripping peak currents, as shown in Fig. 3(b). The plots were linear up to 60 mV and began to decrease thereafter. A pulse amplitude of 60 mV was found to be optimal. Fig. 3(c) shows the influence of the potential on the signal amplitudes. All signals increased linearly up to 6.0 mV, after which they decreased. A potential increment of 6.0 mV was found to be optimal. Thus, the best compromise between achieving adequate sensitivity and reducing the background current was achieved under the following conditions: frequency: 100 Hz; pulse amplitude: 60 mV; potential increment: 6.0 mV.

The effects of the accumulation potential were measured by stepping the potential from −1.20 to −1.30, −1.40, and −1.50 V (vs. Ag/AgCl, not shown). The Zn(II), Cd(II), and Pb(II) stripping peak currents were low at deposition potentials more positive than −1.2 V because these potential values were not sufficiently negative to quantitatively reduce Zn(II), Cd(II), or Pb(II) metal ions in contact with the electrode surface. Within the interval between −1.3 and −1.20 V, the Zn(II), Cd(II), and Pb(II) stripping peak currents remained relatively constant and close to their maximum values (mass-transfer control region). At deposition, potentials more negative than −1.40 V, the Zn(II), Cd(II), or Pb(II) stripping peak currents decreased. This effect was attributed to the release of hydrogen gas that interfered with the smooth deposition of these metal ions onto the electrode surfaces. Therefore, an accumulation potential of −1.40 V was selected as the optimum potential for all subsequent experiments.

The accumulation time effects were measured under a constant accumulation potential of −1.4 V, as shown in Fig. 4. Fig. 4(b) shows that the Zn(II), Cd(II), and Pb(II) stripping peak currents increased in a rectilinear fashion. The increase was almost linear for all

Table 1
The analytical performance of the developed method

Metal ion	Working range (ppb)	The linear regression equation	Regression coefficient	RSD (%) (for *n* = 5)	LOQ (ppb)	LOD (ppb)	WHO TLS (ppb)	EPA TLS (ppb)
Cd(II)	3.0–50	y = 0.0892x	0.9931	2.9	3.0 ± 0.03	1.0 ± 0.03	3.0	5.0
Pb(II)	3.0–50	y = 0.0605x + 0.124	0.9866	3.3	3.0 ± 0.04	2.0 ± 0.04	10.0	15.0
Zn(II)	3.0–50	y = 0.0811x + 0.0862	0.9902	9.9	5.0 ± 0.1	5.0 ± 0.1	300.0	500.0

Table 2
Comparison of the present method for the determination of one of the detected heavy metals, Cd(II), with other anodic stripping techniques at modified electrodes

Electrode substrate	Method	Accumulation potential (V)	Accumulation time (s)	Linear range (ppb)	LOD (ppb)	Refs.
Sb nano/BDDE	LSASV	−1.1	120.0	50.0–500.0	38.10	[32]
Sb/GCE	SWASV	−1.5	120.0	5.0–120.0	1.40	[33]
Bi/PANI/GCE	LSASV	−1.4	240.0	20.0–180.0	1.48	[34]
Sb/CPE	SWASV	−1.2	120.0	5.0–50.0	0.80	[35]
Bi-GC	SWASV	−1.4	120.0	2.0–50	2.0	This work

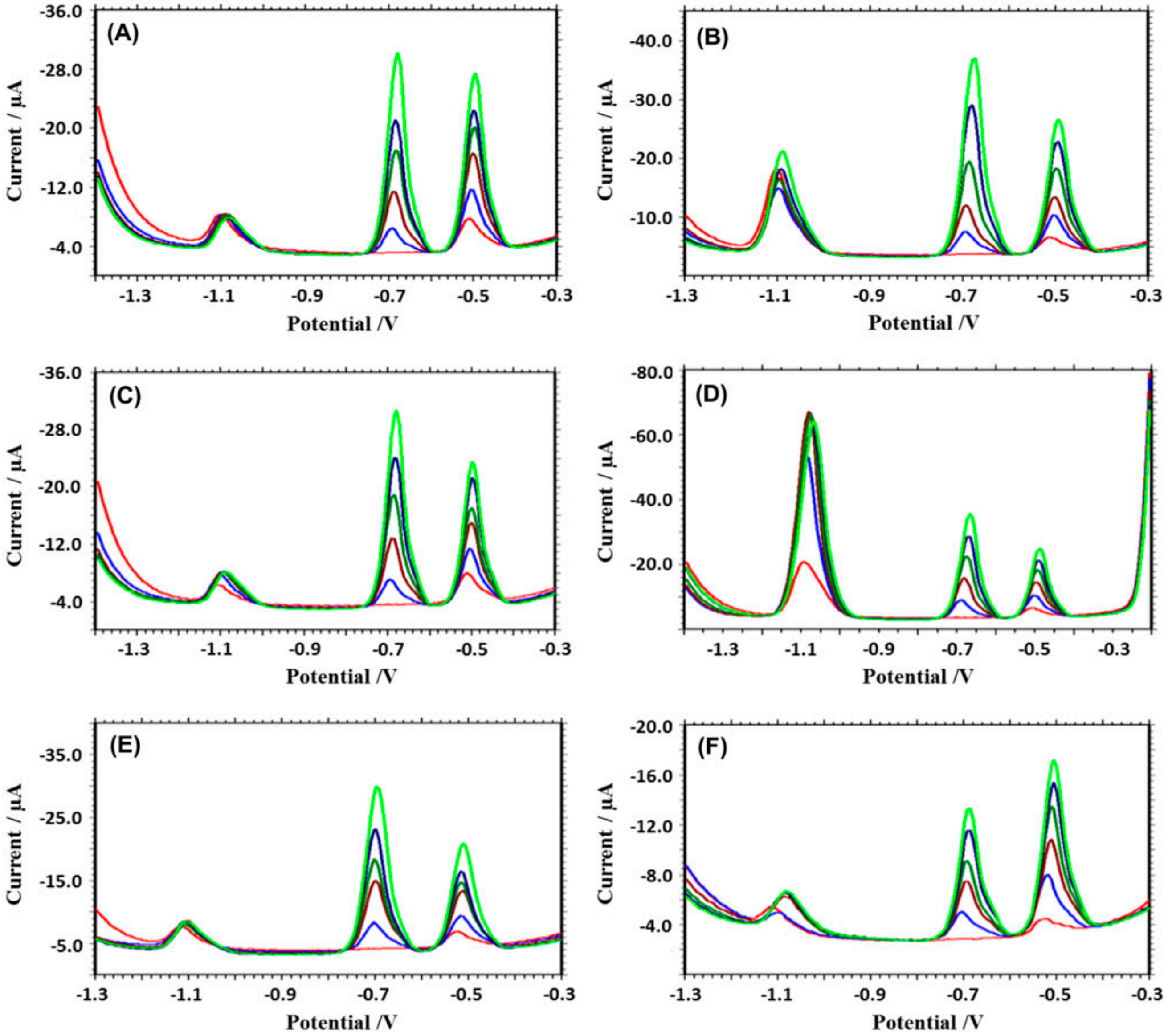

Fig. 7. SWASV of different water samples (A–F) with subsequent additions of 2, 4, 6, 8, and 10 ppb of each of lead(II), cadmium(II), and zinc(II) heavy metals at the GCE-Bi-modified surfaces in acetate buffer solution (0.1 M, pH 3.5); Amplitude, 60 mV; frequency, 100 Hz; potential increment, 8 mV; accumulation time, 2.0 min at −1.4 V. Other conditions are similar to Fig. 5.

Table 3
SWASV and ICP-MS determination of Cd(II), Pb(II), and Zn(II) in drinking water samples

	Cd(II), ppb		Pb(II), ppb		Zn(II), ppb	
Water Sample	SWASV	ICP-MS	SWASV	ICP-MS	SWASV	ICP-MS
1	ND[a]	0.065 ± 0.003	2.2 ± 0.02	2.68 ± 0.03	17.4 ± 0.17	15.80 ± 0.16
2	ND	0.020 ± 0.002	1.3 ± 0.01	1.90 ± 0.02	18.1 ± 0.18	19.26 ± 0.19
3	ND	0.021 ± 0.002	2.3 ± 0.02	2.83 ± 0.03	8.3 ± 0.08	10.35 ± 0.14
4	ND	0.020 ± 0.002	1.4 ± 0.02	1.28 ± 0.01	31.2 ± 0.30	37.89 ± 0.40
5	ND	0.020 ± 0.002	1.5 ± 0.02	0.95 ± 0.01	9.9 ± 0.10	11.97 ± 0.12
6	ND	0.010 ± 0.001	0.7 ± 0.01	0.58 ± 0.01	13.7 ± 0.14	18.59 ± 0.19

[a] Not detected.

three metals with an accumulation time of 300 s. Longer accumulation times provided negligible increases in the peak current. Thus, an accumulation time of 300 s was found to be optimal.

3.3. Calibration study

Under the optimum conditions, a calibration study was completed for the simultaneous determination of Pb (II), Cd(II), and Zn(II) by SWASV. A series of stripping voltammograms were collected over ion concentrations ranging from 1.0 to 50.0 ppb, as shown in Fig. 5.

Fig. 6 shows the corresponding calibration plots with good linearity for all metal ions. The regression equations calculated using the least squares fit are presented in Table 1, along with the corresponding correlation coefficients obtained from each metal.

The limits of detection (LOD), calculated based on a signal-to-noise ratio of 3:1, are listed in Table 1. Considering the threshold limit values (TLV) recommended by the WHO and EPA for Pb(II), Cd(II), and Zn(II) ions in drinking water [27,28], the present method offers a good approach to metal monitoring in drinking water. The measurement precision was evaluated by measuring the stripping responses of samples ($n = 5$) containing different Pb(II), Cd(II), and Zn(II) concentrations.

The obtained results compare well with those reported for the determination of heavy metals (Table 2).

3.4. Sample analysis

Local drinking water samples were collected in high-density polypropylene bottles that had been washed and acidified prior to sample collection. The SWASV technique, along with the standard addition method, was used to test the various drinking water samples using the Bi-modified GCE (Fig. 7). As shown in Table 3, the metal concentrations calculated to be present in the collected water samples did not exceed the recommended EPA or WHO values listed in Table 1. The quantification of these samples was carried out using two techniques, SWASV and ICP-MS, utilizing the standard addition (spiking) method (Table 3). The metal concentrations determined using the two techniques agreed very well, and no significant differences were observed at the 95% confidence level. As demonstrated, all metals were detected at ultra-trace levels, indicating the feasibility of the proposed methodology for use in environmental applications.

4. Conclusions

SWASV was used for the direct and simultaneous determination of Zn(II), Cd(II), and Pb(II) in drinking water samples. After appropriate optimization, the concentrations of the screened metals in drinking water samples were found to fall within the WHO and EPA range for those particular samples and at that specific time. A portable sensor for on-site detection based on the developed and optimized transducer is currently under development in our laboratory to preclude sample collection and transport while enabling on-site sample testing.

Acknowledgments

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