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Individual and simultaneous determination of lead, cadmium, and zinc by anodic stripping voltammetry at a bismuth bulk electrode

Kristie C. Armstrong, Clarissa E. Tatum, Royce N. Dansby-Sparks, James Q. Chambers, Zi-Ling Xue*

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600, USA

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ABSTRACT

A bismuth bulk electrode (BiBE) has been investigated as an alternative electrode for the anodic stripping voltammetric (ASV) analysis of Pb(II), Cd(II), and Zn(II). The BiBE, which is fabricated in-house, shows results comparable to those of similar analyses at other Bi-based electrodes. Metal accumulation is achieved by holding the electrode potential at −1.4 V (vs. Ag/AgCl) for 180 s followed by a square wave voltammetric stripping scan from −1.4 to −0.35 V. Calibration plots are obtained for all three metals, individually and simultaneously, in the10–100 μg L^{-1} range, with a detection limit of 93, 54, and 396 ng L^{-1} for Pb(II), Cd(II), Zn(II), respectively. A slight reduction in slope is observed for Cd(II) and Pb(II) when the three metals are calibrated simultaneously vs. individually. Comparing the sensitivities of the metals when calibrated individually vs. in a mixture reveals that Zn(II) is not affected by stripping in a mixture. However, Pb(II) and Cd(II) have decreasing sensitivities in a mixture. The optimized method has been successfully used to test contaminated river water by standard addition. The results demonstrate the ability of the BiBE as an alternative electrode material in heavy metal analysis.

1. Introduction

Anodic stripping voltammetry is a commonly used technique for trace metal analysis [1]. By holding the electrode at a sufficiently negative potential, the analyte can be reduced to form an amalgam with the electrode, thus pre-concentrating the metal onto the electrode surface. Following pre-concentration, an anodic scan oxidizes the metals, stripping them off of the electrode and yielding a current response that is linear to the metal concentration.

In the past, mercury (Hg)-based electrodes have been the material of choice for stripping analyses due to their attractive analytical properties [1b]. Among these, the extended negative potential window and its ability to form alloys with other metals [1] make mercury an ideal candidate for heavy metal analysis.

Due to the toxicity and inconvenient disposal of Hg, however, alternative electrode materials are being explored. Gold-coated diamond thin film electrodes [2] and boron-doped diamond electrodes [3] have been developed and used in ASV analyses. Among alternative electrode materials, bismuth-based electrodes have been growing in popularity. Bismuth-modified carbon paste electrodes [4], bismuth-modified carbon nanotubes [5], and the widely used bismuth film electrode (BiFE) [6–12] initially developed by Wang and coworkers, share many of the same desirable electrochemical characteristics as Hg-based electrodes. Similar to Hg, Bi is capable of forming fused alloys with heavy metals [13], and exhibits high hydrogen overpotential [14]. In addition to the attractive electrochemical properties, Bi is more environmentally friendly and less toxic.

Among the bismuth-based electrode options, little work has been done using a bismuth bulk electrode (BiBE). Work with a BiBE can, however, offer many advantages. Other Bi-based electrodes can be difficult and time-consuming to fabricate. BiFE films have been shown to be very fragile [15]. The BiBE is easily fabricated, cost-efficient, stable and robust, and is capable of yielding more reproducible results than other previously examined Bi-based electrodes.

Past work with a BiBE has been limited. The use of a BiBE as a substrate for self-assembled monolayers (SAMs) has been examined, allowing for a more negative potential window than SAMs on gold substrates [16]. In addition, a simple method for the creation of Bi nanoparticles has been developed by cathodic dispersion of a BiBE [17]. To date, the BiBE has only been used twice for quantitative analyses. Bučková and coworkers demonstrated the use of the BiBE as a means of enhancing daunomycin detection [18]. Pauliukaite and coworkers characterized the BiBE, and showed its potential use for heavy metal detection [14].

The pioneering studies performed by Pauliukaite and coworkers characterized the electrode, highlighting both its cathodic electrochemical behavior and its behavior under anodic conditions, which causes the formation of a thin, conductive Bi_2O_3 film. The elec-

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* Corresponding author.
E-mail addresses: xue@utk.edu, xue@ion.chem.utk.edu (Z.-L. Xue).

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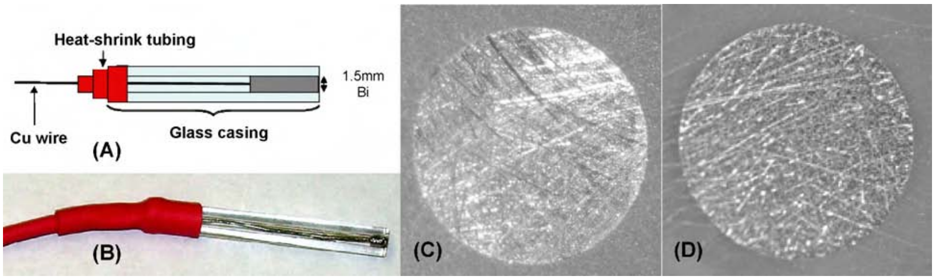

Fig. 1. Bismuth bulk electrode: schematic diagram (A), electrode picture (B), an unpolished electrode surface (C), and a polished electrode surface (D). Images were taken using a Canon PowerShot A630 digital camera and a Cambridge Instruments StereoZoom 7 optical microscope, zoom range of 1.0–7.0×.

trochemistry of various well-known redox couples was inspected and both inorganic and organic compounds were tested at the electrode. The feasibility of the BiBE for use in anodic stripping voltammetry of Pb(II), Cd(II), and Zn(II) was qualitatively shown, thus demonstrating the capability of the BiBE for heavy metal stripping analysis. The only quantitative stripping measurement was that for Pb(II), which resulted in a limit of detection of 3.2 $\mu g\,L^{-1}$. This work provided a basis of understanding and laid the foundation for further studies using the BiBE, as it provided the inspiration for the current studies.

Pb(II), Cd(II), and Zn(II) detection has been performed in the current work using ASV at the BiBE. The BiBE is made in-house by melting bismuth needles into a hand-blown glass casing. All three metals have been quantitatively measured, both individually and in mixtures, with detection limits in the ng L^{-1} range, upon optimization. Extensive studies, with a focus on examining the interactions of the three metals when in a mixture, reveal that, in a mixture, the sensitivity of the metals always drops after the first metal has been stripped. As consecutive metals are stripped, the sensitivity of any remaining metals continues to drop. This shows that, as each metal is stripped, it inadvertently removes portions of any remaining metals adsorbed to the electrode. The potential of this method for use in environmental detection is demonstrated by testing for these metals in river water samples. The method is validated by comparing the results of the samples to those obtained using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

2. Experimental

2.1. Apparatus and reagents

All voltammetric measurements were performed using a modulated potentiostat (CHI 440, CH Instruments). A three-electrode configuration consisted of a BiBE disk (1.5 mm diameter), Ag/AgCl, and a platinum wire as working, reference, and counter electrodes, respectively. The BiBE was made in-house by melting bismuth needles (99.998% purity, Alfa Aesar) into a hand-blown glass casing. The melting process involved placing several rods of bismuth needles into the glass casing. A tin-coated copper wire was inserted partially into the glass casing such that the bismuth would melt around it and would act as the electrical lead. This ensemble was vertically inserted into a glass tube, which was then sealed and connected to a vacuum line. Air from the tube was removed by vacuum and replaced with nitrogen repeatedly to ensure complete removal of the air. The tube was held over a Bunsen burner until the bismuth was melted completely (melting point: 271.5 °C) [19]. This process was done under continuous vacuum to ensure that no air bubbles developed in the sealed tube. After cooling, the electrode was removed from the tubing and the end was cut with a diamond band saw, serving as the surface of the electrode. The freshly exposed electrode surface was polished with a series of emery paper of 200, 400, 600, and 800 grit. Further polishing was done using a standard electrode polishing kit (CH Instruments) that includes a 1200 grit Carbimet disk, 1.0 μm alumina slurry on a nylon cloth, 0.3 μm alumina slurry on a nylon cloth, and 0.05 μm alumina slurry on a microcloth polishing pad. The images in Fig. 1 are a schematic and pictures of the BiBE and its surface. Using a digital ohm meter, the resistance of the fabricated BiBE was measured to be 0.3 Ω.

Acetic acid (glacial, Fisher), sodium acetate (anhydrous, Certified ACS, Fisher), cadmium acetate (Certified ACS, Fisher), and lead nitrate (Certified ACS, Fisher) were used as received. Zn(II) AA standard solution (1000 mg/L, Aldrich) was diluted prior to use. The buffer solution contained 0.1 M sodium acetate and its pH was adjusted to 5.0 with CH_3COOH. Pb(II), Cd(II), and Zn(II) standards (10–100 $\mu g\,L^{-1}$) were prepared by diluting the appropriate amount of stock solution in electrolytes. All aqueous solutions were prepared in 18 MΩ deionized H_2O.

2.2. Procedure

For ASV experiments, 20 mL of standard solutions were used. No deaeration of the samples was required. Square wave voltammetry (SWV) was used for both the accumulation and stripping steps with the following parameters: initial *E*, −1.4 V; final *E*, −0.35 V; increasing *E*, 4 mV; amplitude, 25 mV; frequency, 15 Hz; and quiet time, 180 s. The quiet time was used for the accumulation step, during which the solution was stirred at approximately 1200 rpm. The potential was held constant at the initial potential during the entire quiet time. The SWV scan starts immediately upon completion of the quiet time. No resting period was used between the accumulation and stripping steps. Stirring at high speed was required during the accumulation process but was stopped at the end of the quiet period for the stripping step.

3. Results and discussion

3.1. Individual determination of Pb(II), Cd(II), and Zn(II)

Determination of all three metals was done by making standards containing each of the individual metals. ASV resulted in voltam-

Table 1
R^2 and slope values for Pb(II), Cd(II), and Zn(II) detected simultaneously and individually at the BiBE.

	R^2	Sensitivity ($\mu A\,L\,\mu g^{-1}$)
Individual		
Pb(II)	0.963	0.125
Cd(II)	0.973	0.112
Zn(II)	0.950	0.187
Mixture		
Pb(II)	0.975	0.071
Cd(II)	0.987	0.099
Zn(II)	0.953	0.185

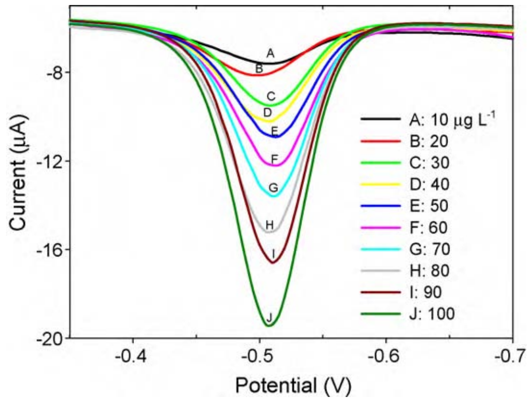

Fig. 2. ASV calibration of Pb(II) detected at the BiBE. Calibrations were conducted using a 1.5 mm BiBE in standards of 10–100 µg L^{-1} of metal ions in 0.1 M sodium acetate at pH 5.0. An accumulation period of 180 s at −1.4 V was used, with stirring at 1200 rpm. Immediately after accumulation, metals were stripped using a SWV scan from −1.4 to −0.35 V.

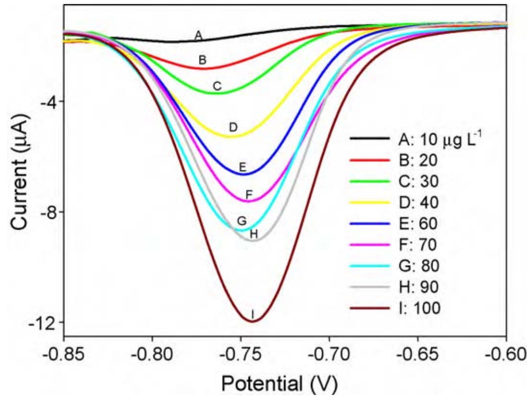

Fig. 3. ASV calibration of Cd(II) detected at the BiBE.

mograms containing peaks corresponding to the oxidation of Pb(0), Cd(0), and Zn(0). The peaks were assigned to each metal by spiking. The peaks for Pb(II) (−0.50 V), Cd(II) (−0.75 V), and Zn(II) (−1.10 V) are in agreement to values found in literature [14]. Figs. 2–4 are the voltammograms for 10–100 µg L^{-1} metals. Calibration plots for the three individual metal solutions give slopes and values of the correlation coefficient R^2 in Table 1.

It is worth noting that, for Cd(II) and Zn(II) analyses in particular, there appears to be a peak potential dependence on concentration. For the Zn(II) analysis, as concentration increases, the peak potential appears to shift in the positive direction. The trend for Cd(II) appears to be the opposite of that observed for Zn(II) – as concentration increases, the peak shifts to a more negative potential. This result suggests that the shift is not due to an IR drop effect.

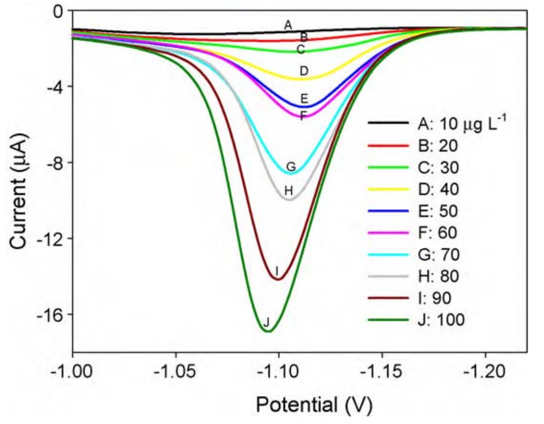

Fig. 4. ASV calibration of Zn(II) detected at the BiBE.

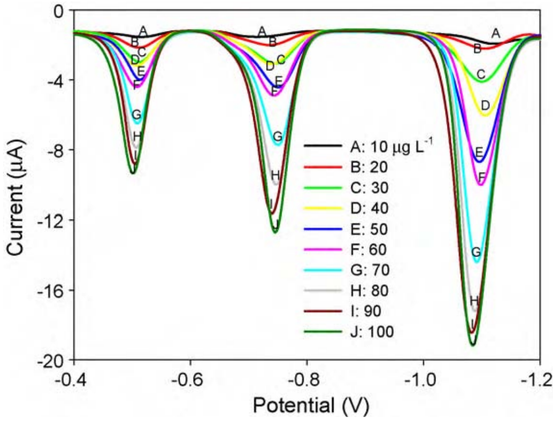

Fig. 5. ASV calibration of mixed metals. The solutions contained Pb(II) (−0.5 V), Cd(II) (−0.75 V), and Zn(II) (−1.10 V).

3.2. *Simultaneous determination of Pb(II), Cd(II), and Zn(II)*

Simultaneous determination of the metals was performed according to the same parameters determined for the individual experiments. Mixtures containing 10–100 µg L^{-1} of each of the three metals were tested. Fig. 5 is a voltammogram of mixtures of Pb(II), Cd(II), and Zn(II). Calibration plots for the three metals in the mixtures give slopes and values of the correlation coefficient R^2 (Table 1).

3.3. *Comparison of individual and simultaneous determination*

Table 1 lists the R^2 values and slopes for the calibration plots of both individual and simultaneous analyses. For both determinations, the E_{peak} values occur at the same potential and R^2 values are similar.

When comparing individual to simultaneous analyses, it is worth noting the sensitivities of each metal calibrated individually vs. in the mixture. The sensitivity of the Zn(II) determination remains relatively unchanged. However, both Cd(II) and Pb(II) sensitivities experience a significant drop when in a mixture. This finding prompted further studies, aimed at examining the interactions among the metals in a mixture.

Thus, a set of experiments was designed such that solutions containing individual metals were compared against solutions containing all three metals, with varying accumulation potentials. Solutions containing the individual metals were tested with an accumulation potential slightly more negative than their respective stripping peak potentials. The accumulation potentials were held at −0.6, −0.9, and −1.2 V for Pb(II), Cd(II) and Zn(II) solutions, respectively. Solutions containing all three metals (20–100 µg L^{-1} each) were also tested at accumulation potentials of −0.6, −0.9, and −1.2 V, and compared to the individual metals. Aside from varying accumulation potentials, all electrochemical parameters for testing remained the same as was used for the SWV calibrations mentioned earlier in this paper.

Results of these tests are shown in Table 2. When comparing the sensitivities of individual metal calibrations to the sensitivities of mixed metal calibrations, a significant change in slope is only observed in a certain metal if another metal was stripped prior to that particular metal. If the accumulation potential of a metal in a mixture was such that the metal of interest was stripped first,

Table 2
Deposition potential and stripping sensitivities of Pb(II), Cd(II), and Zn(II) individually vs. in a mixture.

	Deposition potential (V)	Sensitivity (μA L μg^{-1})
Individual		
Pb(II)	−1.4	0.125 ± 0.008
Pb(II)	−0.6	0.030 ± 0.003
Cd(II)	−1.4	0.112 ± 0.005
Cd(II)	−0.9	0.0055 ± 0.0005
Zn(II)	−1.4	0.187 ± 0.017
Zn(II)	−1.2	0.038 ± 0.008
Mixture		
Pb(II)	−1.4	0.071 ± 0.007
Pb(II)	−0.6	0.026 ± 0.001
Cd(II)	−1.4	0.099 ± 0.010
Cd(II)	−0.9	0.0042 ± 0.0008
Zn(II)	−1.4	0.185 ± 0.012
Zn(II)	−1.2	0.037 ± 0.005

then its sensitivity remains roughly the same as compared to an individual calibration.

For instance, the stripping sensitivity of Pb(II) calibrated individually, with an accumulation potential of −0.6 V, is 0.030 ± 0.003 μA L μg^{-1}. In a mixture containing Pb(II), Cd(II), and Zn(II), with an accumulation potential of −0.6 V, the stripping sensitivity for Pb(II) is 0.026 ± 0.001 μA L μg^{-1}. This sensitivity is within the range of deviation of the Pb(II) stripping sensitivity in the individual calibration. This is because, at an accumulation potential of −0.6 V, no Cd(II) or Zn(II) are being accumulated; thus no Cd(0) or Zn(0) are being stripped. However, when the accumulation potential is set to −1.4 V, the stripping sensitivity of Pb(II) individually is 0.125 μA L μg^{-1}, vs. a sensitivity of 0.071 μA L μg^{-1} in a mixture. At an accumulation potential of −1.4 V, all three metals, Pb(II), Cd(II), and Zn(II), are accumulated and stripped. Zn(0) and Cd(0) are stripped off before Pb(0), and in the process of stripping, are also removing a significant portion of the accumulated Pb(0), as well, causing a 43% drop in sensitivity for Pb(II), in this particular case. A similar trend for Cd(II) can be observed, and the sensitivity for Zn(II) stripping remains relatively unchanged when calibrated individually vs. in a mixture.

It can be noted that, as is well known for ASV, the sensitivity is a strong function of the deposition potential. Accordingly, the river water analyses described below were carried out using a standard addition protocol and a deposition potential of −1.4 V.

Another factor that could account for the differences in slopes between simultaneous and individual calibrations is the interactions among the heavy metals when placed together in a mixture. Work by Manivannan et al. showed that, in the presence of Pb(II), peak currents for Cd(II) were cut in half, as compared to a calibration of Cd(II) alone [20]. Thus, it can be assumed that, in a mixture, interactions among various heavy metals can diminish the current response for each metal.

3.4. Optimization of the analytical signal

Different accumulation times were tested for optimal peak formation. An accumulation time of 180 s was found to be best. At times lower than this, peak heights were lower; at longer accumulation times, the peaks became distorted, possibly due to saturation of the electrode.

Stirring was another important issue that was studied. Slow stirring resulted in much smaller peaks than stirring at full speed. This is due to the increased convective mass transport to the electrode surface.

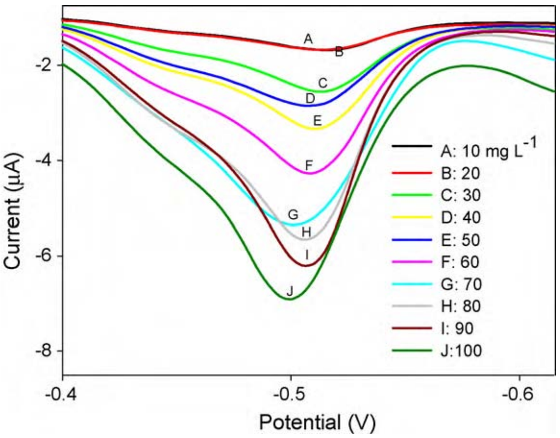

Fig. 6. ASV calibration of Pb(II) at the BiBE after 30 consecutive runs. A 1.5 mm BiBE was used in standards ranging from 10 to 100 μg L^{-1} Pb(II) in 0.1 M sodium acetate at pH 5.0. An accumulation period of 180 s at −1.4 V was used, with a stirring at 1200 rpm. Immediately after accumulation, metals were stripped using a SWV scan from −1.4 to −0.35 V.

3.5. Electrode stability

After extensive use of the BiBE for multiple runs, misshapen and broad peaks were observed, as shown in Fig. 6. Upon examination, the BiBE surface, which, upon fresh polishing has a metallic luster, appeared dull with some black spots after multiple runs. This is believed to be the formation of a bismuth oxide [17,21,22]. A Pb(II) calibration run at a freshly polished BiBE (Fig. 2) shows a single, well-defined peak. The presence of the double peak for Pb(II), which is observed only after extensive use of the BiBE, indicates that the BiBE surface was altered by the suspected oxide formation. The double peak suggests that Pb(II) exists in two different adsorption states, perhaps associated with the formation of the bismuth oxide. From these data, it is estimated that 30 samples could be run consecutively before the altered state of the electrode distorts the ASV response. At this point, an additional polishing step would be needed to regenerate the electrode surface. This is comparable to Pb(II), Cd(II), and Zn(II) analyses done at other electrodes. Kefala and coworkers stated that only small drifts in peak height were observed after 20 consecutive measurements at a Nafion-coated BiFE, indicating satisfactory stability [30]. Similar results were observed by Lee and coworkers [25]. Twenty consecutive measurements of 30 μg L^{-1} of Pb(II) and Cd(II) at a Bi nanopowder electrode resulted in very low RSDs.

3.6. Dynamic range and detection limits

Using a 180 s accumulation time, the limit of detection calculated for each metal (3σ, $n = 5$) is 93 ng L^{-1} for Pb(II), 54 ng L^{-1} for Cd(II), and 396 ng L^{-1} for Zn(II) for the 1.5 mm diameter electrode. The dynamic range was 10–100 μg L^{-1} for all metals.

When comparing this work to Pb(II), Cd(II), and Zn(II) analyses done in the past by others, it appears that the BiBE offers one of the lower detection limits for these metals. Table 3 summarizes past work on ASV of Pb(II), Cd(II), and Zn(II) at various electrodes.

Some recent research efforts have focused on the on-line combination of electrochemistry for pre-concentration with detection by, e.g., ICP-MS for various heavy metals as a means of enhancing sensitivity over traditional spectroscopic techniques [32,33]. ASV, generally at a thin film mercury electrode, serves to enhance the signal by pre-concentrating the metals onto the electrode surface. Immediately following pre-concentration, an oxidative scan is performed, stripping the metals from the surface. This solution is diverted out of the electrochemical flow cell and into a cell used

Table 3
Summary of past efforts on ASV detection of Pb(II), Cd(II), and/or Zn(II) at various electrodes.

Author	Detected metals	Electrode type	Accumulation time and potential	Electrochemical stripping technique	Detection limit ($\mu g\,L^{-1}$)	Reference #
Rico et al.	Pb(II), Cd(II), Zn(II)	Bi nanoparticles on screen-printed C	−1.4 V, 120 s	SWASV	Pb(II) = 0.9 Cd(II) = 1.3 Zn(II) = 2.6	[23]
El Tall et al.	Pb(II), Cd(II), Zn(II), Cu(II)	B-doped diamond	−1.7 V[a], 60 s	DPASV	Pb(II) = 1.15 Cd(II) = 0.36 Zn(II) = 1.6	[3]
Rehacek et al.	Pb(II), Cd(II), Zn(II)	Disc graphite BiFE	−1.3 V, 120 s	SWASV	Pb(II) = 0.497 Cd(II) = 0.325 Zn(II) = 0.785	[24]
Lee et al.	Pb(II), Cd(II)	Bi nanopowder on C	−1.2 V, 3 min	SWASV	Pb(II) = 0.15 Cd(II) = 0.07	[25]
Svancara et al.	Pb(II), Cd(II)	Bi film-C paste	−0.95 V, 120 s	SWASV	Pb(II) = 0.8 Cd(II) = 1.0	[4]
Hwang et al.	Pb(II), Cd(II), Zn(II)	Bi-C nanotube	−1.4 V[a], 300 s	SWASV	Pb(II) = 1.3 Cd(II) = 0.7 Zn(II) = 12	[5]
Wu et al.	Pb(II), Cd(II), Zn(II)	Bi/poly(p-ABSA)	−1.4 V, 240 s	DPASV	Pb(II) = 0.80 Cd(II) = 0.63 Zn(II) = 0.62	[26]
McGraw et al.	Pb(II), Cd(II), Zn(II), Cu(II), Ag(I)	B-doped diamond	−0.8 V (Pb), −1.0 V (Cd), −1.3 V (Zn)	DPASV	Pb(II) = 5.0 Cd(II) = 1.0 Zn(II) = 50	[27]
McGraw et al.	Pb(II), Cd(II), Zn(II), Cu(II), Ag(I)	MFE	−0.8 V (Pb), −1.0 V (Cd), −1.3 V (Zn)	DPASV	Pb(II) = 5.0 Cd(II) = 1.0 Zn(II) = 10	[27]
Siriangkhawut	Pb(II), Cd(II)	BiFE	−1.10 V, 90 s	SWASV	Pb(II) = 6.9 Cd(II) = 1.4	[28]
Torma et al.	Pb(II), Cd(II), Zn(II)	NC(Bpy) BiFE	−1.4 V, 2 min	SWASV	Pb(II) = 0.077 Cd(II) = 0.12 Zn(II) = 0.56	[29]
Kefala et al.	Pb(II), Cd(II), Zn(II)	NC BiFE	−1.40 V	SWASV	Pb(II) = 2 Cd(II) = 2 Zn(II) = 6	[30]
Tesarova et al.	Pb(II), Cd(II)	Sb-CPE	−1.2 V, 120 s	SWASV	Pb(II) = 0.2 Cd(II) = 0.8	[31]

[a] Potential vs. SCE.

for MS or ICP-MS detection. The coupling of electrochemical preconcentration on a mercury electrode with MS or ICP-MS has been shown to greatly enhance the sensitivity over traditional spectroscopic methods, improving the signal-to-noise ratio by factors up to 11 [32]. In comparison with our results here, it seems that this pairing does appear to enhance the detection limit over traditional electrochemical techniques alone. A detection limit of 0.16 $ng\,L^{-1}$ was obtained for Cd(II) using this combination [32], which is lower than any electrochemical technique currently known, and far lower than the detection limit (1 $\mu g\,L^{-1}$) attainable by ICP-MS alone. It should be noted that this technique used a pre-concentration time of 340 s vs. 180 s in the current work. Also, sophisticated instrumentation, plus flow cells and high efficiency nebulizers to connect the two different instruments, are needed to achieve the detection limit of 0.16 $ng\,L^{-1}$. In comparison, the current work requires a simple standard electrochemical cell.

3.7. *Analytical application of the BiBE in river water samples*

The BiBE was used to determine the Pb(II), Cd(II), and Zn(II) levels in two separate river water samples. The first sample was obtained from the Tennessee River in Knoxville, TN. The second sample was from the Emory River, located near Harriman, TN, obtained shortly after contamination from a massive coal fly ash spill [34]. Prior to analysis, the river water was acidified by nitric acid and filtered, with standard filter paper, to remove non-dissolved solids. Sodium acetate buffer was made by dilution in the treated river water. The pH was then adjusted to 5.0 with ammonium hydroxide. Standard additions of Pb(II), Cd(II), and Zn(II) were added, individually, to the river water, to a total volume of 25 mL. Pb(II) additions ranged from 0 to 12 $\mu g\,L^{-1}$, Cd(II) from 0 to 4 $\mu g\,L^{-1}$, and Zn(II) from 0 to 120 $\mu g\,L^{-1}$. After a 240 s accumulation period, SWV was used for a stripping analysis as described above.

For the sample obtained from the Tennessee River, no Pb(II), Cd(II), or Zn(II) was found. It can be assumed that the quantity of each of these three metals in the sample was below the detection limit of the BiBE.

For the contaminated river water, obtained from the Emory River, peaks corresponding to Pb(II) and Zn(II) were observed, but no peak for Cd(II) was seen. A Cd(II) standard addition was run, again, on the same sample of water, using a larger concentration range of standards (0–100 $\mu g\,L^{-1}$), obtaining an estimated Cd(II) concentration of 2.98 ± 6.0 $\mu g\,L^{-1}$. Thus, it can be assumed that no Cd(II) is present in this particular river water sample. For the Zn(II) standard addition, the peak was misshapen and broad, resulting in poor linearity ($R^2 = 0.5297$). It can be assumed that, since the water was contaminated with a number of heavy metals and various other impurities, the presence of an interfering species prevented effec-

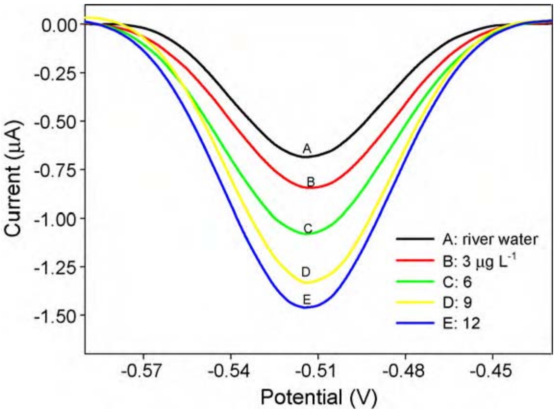

Fig. 7. ASV of Pb(II) standard addition at the BiBE. Concentration of the Pb(II) additions ranged from 0 to 12 μg L^{-1}.

Table 4
Comparison of ICP-OES and ASV analysis of Pb(II) using standard addition.

	[Pb(II)] (μg L^{-1})	R^2
ASV analysis	8.69 ± 0.72	0.9665
ICP-OES	7.79 ± 0.48	0.9628

tive detection of Zn(II). Standard addition of Pb(II) (Fig. 7) yielded an estimated concentration of 8.69 ± 0.72 μg L^{-1}.

Electrochemical results for Pb(II) were validated using ICP-OES, which gave a concentration of 7.79 ± 0.48 μg L^{-1} (Table 4). In the range from 0 to 4 μg L^{-1}, linearity of Cd(II) analysis was poor. The detection limit of the instruments is not sensitive enough for reliable analysis in that particular range. Thus, this does match electrochemical results, and confirms that a negligible amount of Cd(II) is present in this particular water sample.

These results show that the potential applications of this electrode will depend on the nature of the sample being analyzed. In a normal river water sample, such as that obtained from the uncontaminated Tennessee River, the levels of Pb(II), Cd(II), and Zn(II) are lower than the detection limits for both this electrode and ICP-OES. For analyses of this type of sample, where only ultra-trace levels of the analyte exist, a more sensitive technique will need to be employed. The BiBE is better suited for analyses in samples containing higher concentrations of the metal ions, such as water from the heavily contaminated Emory River. Even in cases such as this, the possibility of interfering species, as with Zn(II) in our contaminated water sample, should be considered and evaluated prior to analyses. By using a standard addition method for sample quantification, matrix effects are significantly diminished, allowing for the potential application of the BiBE to the detection of many other metal ions.

4. Conclusions

The BiBE has been shown as a useful sensor for Pb(II), Cd(II), and Zn(II), with detection limits in the ng L^{-1} range. The parameters for accumulation time and stirring were optimized. Calibrations resulted in good linearity for solutions containing not only the individual metals, but also all three metals at once, demonstrating the potential use of the BiBE as a multi-sensor for heavy metals. By analyzing river water samples, the capability of the BiBE for use in environmental analysis was demonstrated. Due to its inexpensive and easy fabrication, and extended electrode stability, the electrode is a desirable option for heavy metal sensing, while avoiding the toxicity associated with mercury-based electrodes.

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