Electroanalytical Determination of Cadmium(II) and Lead(II) Using an *in-situ* Bismuth Film Modified Edge Plane Pyrolytic Graphite Electrode

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A highly sensitive and simple electroanalytical methodology is presented using an *in-situ* bismuth film modified edge plane pyrolytic graphite electrode (BiF-EPPGE) which is exemplified with the simultaneous determination of cadmium(II) and lead(II). Square-wave anodic stripping voltammetry is utilised with the effects of several experimental variables studied. Simultaneous additions of cadmium(II) and lead(II) were investigated where two linear ranges between 0.1 – 100 and 0.1 – 300 μg/L and also detection limits of 0.062 and 0.084 μg/L were obtained, respectively. The method was then successfully applied to the simultaneous determination of cadmium(II) and lead(II) in spiked river water, where recoveries of 100.5 and 98% were obtained, respectively. This electroanalytical protocol using edge plane pyrolytic graphite electrodes is one of the simplest methodologies to date using non-mercury based electrodes and is simpler and cheaper than alternatives such as carbon nanotube electrode arrays, suggesting the use of edge plane pyrolytic graphite electrode for routine sensing.

Cadmium(II) and lead(II) which occur in close association in nature are known to be hazardous environmental pollutants with toxic effects on living organisms. Nevertheless they have been used extensively in industry in the production of pigments, anti-corrosion coatings, alloys, batteries *etc*.[1] Substantial amounts of lead(II) and cadmium(II) are continuously added to air, water and soil as a consequence of human pollution. Lead(II) and cadmium(II) are also of great toxicological interest due to their accumulation in soft tissues, in association with metal binding proteins. For these reasons the measurement of cadmium(II) and lead(II) is becoming more important in industrial, clinical and toxicological laboratories.[2]

Stripping voltammetric techniques are well known as very powerful techniques for determination of diverse range of metallic and biological targets in environmental, biological and industrial samples. Their significant sensitivity is due to their unique ability to preconcentrate target species during the preconcentration step and its combination with pulse measurement techniques that generates a highly favorable signal-to-background ratio. Mercury based electrodes such as, mercury film electrodes and hanging mercury drop electrodes, have been traditionally used in stripping techniques because of their advantages such as high sensitivity, reproducibility, purity of the surface, high hydrogen overpotential, and possibility of amalgam formation and they have been recognized as the most sensitive electrodes for determination of heavy metals.[3,4] But despite the excellent performance of mercury based electrodes for different applications, because of the inconvenience in handling mercury and the well-known toxicity of mercury, its application is unfavored and its use as an electrode material may severely become restricted or even banned in the future regulations and occupational health considerations.[5]

In the last few years, bismuth-film electrodes, consisting of a deposited thin film of bismuth on the surface of some solid electrodes, have been shown to offer comparable performances to mercury film electrodes in stripping voltammetric techniques. It has been shown that bismuth film electrodes have the same advantages as mercury film electrodes and at the same time, due to the negligible toxicity of bismuth, they are also environmentally friendly.[6-8] Various types of bismuth modified electrodes have been utilized for the determination of heavy metals using stripping analysis methods. Bismuth is used for the modification of different kinds of carbon based electrodes such as carbon paste electrodes,[6,9-11] carbon fiber electrodes,[8] graphite epoxy composite electrodes,[12,13] carbon nanotube nanoelectrode array,[14] carbon film electrodes,[15,16] boron doped diamond[17] and particularly glassy carbon electrodes.[18-35] It is also used for modification of other types of electrode materials such as screen printed electrodes,[36,37] copper disk electrodes,[38-40] pencil lead(II) electrode[41] and electrically heated electrode[42] and they are used for detection of different heavy metal ions such as cadmium,[12,14,21,24,26] lead,[12,21,27,29] zinc,[20,26,27] nickel,[23,28,34] cobalt,[23,24,28] indium,[21,30] thallium,[30] tin,[19] chromium[35] and manganese.[17]

Edge plane and basal plane pyrolytic graphite electrodes are fabricated from highly ordered pyrolytic graphite (HOPG). The basal plane surface of an HOPG electrode consists of layers of graphite which lie parallel to the surface and with an interlayer spacing of 3.35 Å. Surface defects occur in the form of steps exposing the edges of the graphite layers. Due to the nature of the chemical bonding in graphite, the two planes, edge and basal, exhibit completely different properties. For electrochemistry, the edge plane exhibits considerably faster electrode kinetics in comparison with the basal plane.[43,44] This means that in many instances an electrode consisting entirely of edge plane *viz*. edge plane pyrolytic graphite (EPPG) electrode

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Table 1   Present work comparison with previous work from bismuth modified electrodes used for determination of cadmium(II) and lead(II)

Bi-modified electrode	Deposition time/s	Cadmium(II)		Lead(II)		Ref.
		LOD/μg L^{-1}	LDR/μg L^{-1}	LOD/μg L^{-1}	LDR/μg L^{-1}	
EPPGE (present work)	240	0.062	0.1 – 100	0.084	0.1 – 300	
Carbon paste	120	1	2 – 20	0.8	2 – 20	6
Copper RDE	300	0.68	2 – 12	0.62	2 – 18	39
CNT nanoelectrode array	240	0.04	0.5 – 8	—	—	14
Graphite epoxy composite electrode	120	7.2	10 – 90	11.81	10 – 70	12
Copper	900	≈11.24	≈11.24 – 112.4	—	NA	40
Graphite epoxy composite electrode	120	2.2	15 – 90	23.1	15 – 90	13
Carbon paste	60	1.2	10 – 100	0.9	10 – 100	9
Carbon film	120	≈0.12	≈4.5 – 39.3	≈0.13	≈4 – 14	16
Glassy carbon RDE	180	0.1	1 – 20	0.1	1 – 20	22
Bismuth bulk	120	—	—	3.2	10 – 200	49
Pencil-lead (sic)	120	0.3	2 – 24	0.4	2 – 24	41
Screen-printed	120	8	20 – 300	10	20 – 300	36
Glassy carbon	10 min	0.2	2 – 18	0.2	2 – 18	27
Carbon and Pt microdisks	180 – 480	—	≈1.12 – 56.2	—	≈2 – 104	7
Glassy carbon	300	0.2	20 – 200	0.8	20 – 200	29
Heated carbon paste	120	—	—	3.16	20 – 140	42
Glassy carbon	120	—	10 – 80	—	10 – 80	30
Screen printed	120 – 600	—	—	0.3	10 – 200	37
Carbon fibre	600	—	—	0.3	40 – 200	8

LOD, limit of detection; LDR, linear dynamic range.

will show a nearly electrochemically reversible voltammogram while an electrode consisting mainly of basal plane will show irreversible behaviour depending highly on the amount of edge plane sites.[43,44] Another fascinating form of carbon is carbon nanotubes (CNTs). CNTs are concentric graphitic cylinders which may be closed at either end due to the presence of five-membered rings. In contrast, glassy carbon is comprised of a structure of interwoven ribbons of the graphite structure. This structure means glassy carbon is a much harder form of graphite, and it is impermeable to liquids or gases.

In the present paper, highly sensitive and simultaneous determination of cadmium(II) and lead(II) on a bismuth film modified edge plane pyrolytic graphite electrode (BiF-EPPGE) using square-wave anodic stripping voltammetry is reported. This modified electrode is a valuable alternative for mercury-based electrodes for anodic striping voltammetric determination of cadmium(II) and lead(II). There are a wide variety of literatures regarding various electrochemical methods and electrodes for simultaneous or individual determination of cadmium(II) and lead(II); but electrochemical determination of cadmium(II) and lead(II) using different types of bismuth modified electrodes are summarized in Table 1. As can be seen in Table 1, earlier electrochemical procedures using bismuth modified electrodes suffered from relatively high detection limits[12,13] and/or limited linear dynamic ranges[14] and/or difficult handling in the process of electrode manufacturing or modification.[12,14,39]

Experimental

Chemicals and apparatus

All chemicals used were of analytical grade and were used as received without any further purification. These were bismuth(III) nitrate hydrate (99.99+%, Alfa Aesar), cadmium(II) nitrate tetrahydrate (99.0%, BDH), lead nitrate (99.5%, BDH). All solutions were prepared with deionized water of resistivity not less than 18.2 MΩ cm^{-1} (Vivendi Water

Systems, UK). Voltammetric measurements were carried out using a μ-Autolab II (ECO-Chemie, The Netherlands) potentiostat. All measurements were conducted using a three electrode configuration. A 4.9 mm (diameter) edge plane pyrolytic graphite electrode (EPPGE, Le Carbone, Ltd., Sussex, UK), was used as the working electrode. For the EPPGE electrode, discs of pyrolytic graphite were machined to 4.9 mm diameter, which was oriented with the disc face parallel with the edge plane as required. The EPPGE electrode was polished before each experiment with alumina (Buehler, USA). A saturated calomel electrode (SCE) (Radiometer, Copenhagen, Denmark) was used as reference electrode and the counter electrode was a bright platinum wire.

Procedure

The edge plane pyrolytic graphite electrode (EPPGE) was polished with hand or polishing machine using slurry of alumina (decreasing size from 5 to 0.1 μm) and rinsed with deionized water before experiments. Then normally the EPPGE was placed in a 0.1 M acetate buffer solution (pH 4.5) containing 1 mg/L Bi(III), and target metal ions such as cadmium(II) and/or lead(II). Next a deposition potential of –1.2 V for 240 s and then 10 s equilibration time without applying potential to relax the electrode surface after deposition of species. Before each voltammogram, a conditioning potential of +0.8 V was applied to the electrode for 90 s to remove any probable memory effects of previous experiments on the electrode surface. These conditions were utilised for experiments after optimization process; during optimization each of these variables were changed one by one.

Results and Discussion

Development of a bismuth film modified edge plane pyrolytic graphite electrode

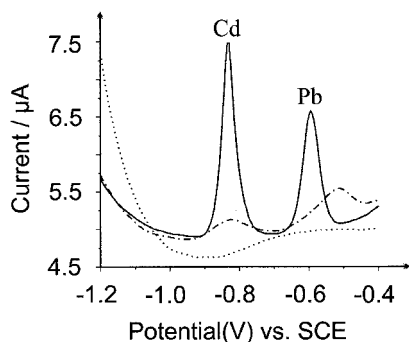In order to evaluate the applicability and effectiveness of

Fig. 1   Blank signal for EPPG electrode in 0.1 M acetate buffer (dotted line).   Anodic stripping voltammograms for 25 μg/L cadmium(II) and 25 μg/L lead(II) on EPPG electrode in 0.1 M acetate buffer pH 4.5 in the absence of Bi(III) (dashed dotted line).   Anodic stripping voltammograms for 25 μg/L cadmium(II) and 25 μg/L lead(II) on EPPG electrode in 0.1 M acetate buffer pH 4.5 in the presence of 1 mg/L Bi(III) (solid line).

bismuth film modified edge plane pyrolytic graphite electrode for cadmium(II) and lead(II) detection, we examined two different test solutions. The first solution was a 0.1 M acetate buffer solution pH 4.5 containing 25 μg/L Cd(II), 25 μg/L Pb(II) and 1 mg/L Bi(III), while the second solution was without Bi(III). The EPPGE was immersed in both solutions following with deposition at a potential of –1.2 V for 240 s and equilibration time of 10 s without applying potential in order to relax the electrode surface. Square-wave anodic stripping voltammetry was then utilised for the detection of cadmium(II) and lead(II) in both solutions with scanning the potential from –1.2 to –0.4 V. The dotted line in Fig. 1 shows the blank signal for an EPPG electrode in 0.1 M acetate buffer pH 4.5 while the dashed-dotted line and the solid line in Fig. 1 present square wave anodic stripping voltammograms of cadmium(II) and lead(II) on bare-EPPGE and BiF-EPPGE, respectively. As can be seen, small and broad stripping peaks are observed for cadmium(II) and lead(II) at potentials of *ca*. –0.84 and *ca*. –0.51 V (*versus* SCE) at the bare-EPPG electrode (dashed-dotted line in Fig. 1) while larger peaks are observed for cadmium(II) and lead(II) using the BiF-EPPG electrode (solid line in Fig. 1). The increase in oxidative current at the BiF-EPPG electrode, demonstrates that the bismuth film which is deposited on the electrode surface plays an important role in the accumulation process of cadmium(II) and lead(II) on the electrode surface. In the electrodeposition step, bismuth and target metals can nucleate on the edge plane sites on the surface of electrode and form an alloy[12,13,17,20] that can be anodically stripped in the stripping step resulting in well defined peaks for lead(II) and cadmium(II).

Characterization of electrode surface

   Formation of amalgam is the factor responsible for the good stripping performance of mercury based electrodes, while the attractive and unique behaviour of bismuth film electrodes is due to the formation of binary or multicomponent alloys.[5] Bismuth forms binary or multicomponent (low-temperature melting) alloys with heavy metals such as cadmium, lead, indium, antimony, thallium or gallium. The formation of this type of low-temperature alloys facilitates the nucleation process during the deposition of heavy metals.[5]

   Figure 2A shows the AFM image of bare EPPG electrode. From this figure it is evident that the surface of EPPG electrode is relatively rough compared to other carbon based electrodes
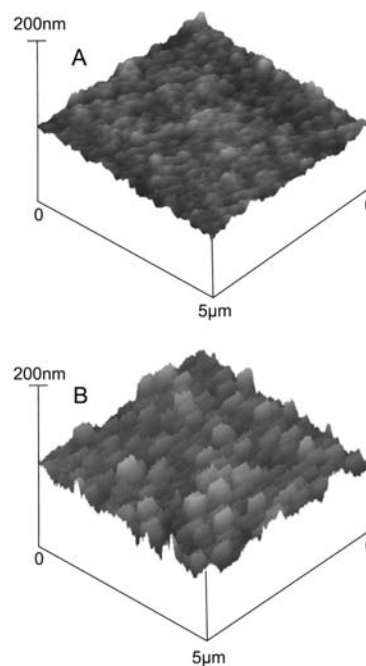

Fig. 2   AFM image of the surface of a bare EPPG electrode (A) and AFM image of the surface of EPPG electrode after electrodeposition of Bi(III) (B) by applying the potential of –1.2 V for 240 s to an EPPGE in a 0.1 M acetate buffer pH 4.5 containing 1 ppm Bi(III).

such as boron-doped diamond and glassy carbon electrodes. Figure 2B shows an AFM image of the surface of an EPPG electrode after the electrodeposition of Bi(III) ions at a potential of –1.2 V for 240 s. In Fig. 2B, the formation of nucleated bismuth on the surface of the electrode can be observed, in comparison to Fig. 2A, which indicates the possibility of formation of a bismuth film, however further meaningful insights are precluded due to the inherent roughness of the edge plane pyrolytic graphite surface.

Optimization of parameters

   In order to optimize the conditions for the simultaneous determination of cadmium(II) and lead(II), the effect of different parameters such as Bi(III) concentration, deposition potential, deposition time, conditioning potential and conditioning time was investigated. At first, the effect of varying the Bi(III) concentration between 0.01 and 10 mg/L on the magnitude of the stripping peaks of cadmium(II) and lead(II) was investigated. The Bi(III) concentration was changed over the range 0.01 to 1 mg/L and the cadmium(II) and lead(II) signals were observed to increase significantly. After additions of more Bi(III), the peaks were observed to decrease in size to half of their original magnitude. The increasing trend of the cadmium(II) and lead(II) signals in concentrations between 0.01 and 1 mg/L is attributed to the increased number of nucleation sites and alloy formation on the electrode surface. The reduction of cadmium(II) and lead(II) signals in concentrations higher than 1 mg/L is likely due to formation of a thick layer of bismuth on the electrode surface that partially blocks the conductive surface of the electrode reducing the number of sites where the extent of three phase boundary occurs, and resulting in the observed decrease in the current density.   A concentration of 1 mg/L was the optimized concentration of Bi(III) for the analytical procedure.

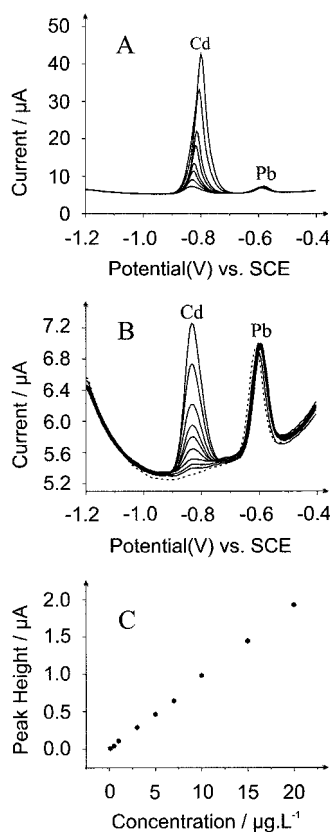   Next the effect of the deposition potential on the cadmium(II)

Fig. 3   (A) Anodic stripping voltammograms for the second linear range of calibration curve for additions of 20, 30, 40, 50, 75, 100, 150 and 200 µg/L Cd(II) on EPPG electrode in 0.1 M acetate buffer pH 4.5 in the presence of 30 µg/L Pb(II) and 1 mg/L Bi(III). (B) Anodic stripping voltammograms for the first linear range of calibration curve for additions of 0.1, 0.5, 1, 3, 5, 7, 10, 15 and 20 µg/L Cd(II). (C) First linear range of calibration curve for additions of Cd(II).

Fig. 4   (A) Anodic stripping voltammograms for the second linear range of calibration curve for additions of 30, 40, 50, 75, 100, 150 and 200 µg/L Pb(II) on EPPG electrode in 0.1 M acetate buffer pH 4.5 in the presence of 40 µg/L Cd(II) and 1 mg/L Bi(III). (B) Anodic stripping voltammograms for the first linear range of calibration curve for additions of 0.2, 1, 3, 5, 7, 10, 15, 20 and 30 µg/L Pb(II). (C) First linear range of calibration curve for additions of Pb(II).

and lead(II) stripping signals was investigated by varying the potential between –0.7 and –1.5 V. The signals of cadmium(II) and lead(II) increased on varying the potential over the range –0.7 to –1.0 V which reached a maximum at –1.2 V. In potentials more negative than –1.2 V, the signals were diminished slightly probably due to hydrogen evolution and bubble formation on the electrode surface. The potential of –1.2 V was therefore selected as the optimum deposition potential for the simultaneous determination of cadmium(II) and lead(II).

The dependence of the anodic stripping signals of cadmium(II) and lead(II) from applying various deposition times between 0 and 300 s was also investigated. The peak current of the voltammetric stripping signals was found to increase significantly on increasing the deposition time over the range 0 to 300 s, indicating an enhancement of cadmium(II) and lead(II) deposition at the electrode surface. A deposition time of 240 s was ultimately used for further experiments as a compromise between relatively short analysis time and high sensitivity.

In order to remove any probable memory effects of previous experiments on the electrode surface before each voltammogram, a conditioning potential was applied to the EPPG electrode. The effect of the conditioning potential and time was investigated for the detection of cadmium(II) and lead(II) and the most reproducible signals were obtained in potential of +0.8 V and time of 90 s, which therefore were selected as optimum for further experiments. According to the
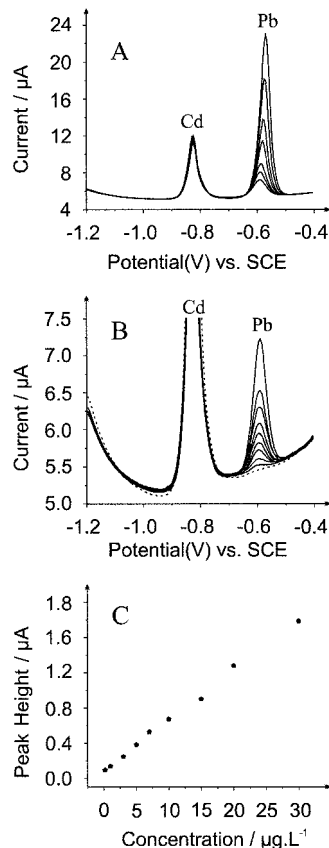
literature, 0.1 M acetate buffer solution pH 4.5 has been the most appropriate supporting electrolyte for detection of cadmium(II) and lead(II) on Bi-film modified electrodes,[9,12-14,16,27,29,30,41] therefore we used it as optimum supporting electrolyte in all of our experiments in this paper.

Calibration data

After optimization of different parameters, additions of cadmium(II) and lead(II) using optimized conditions were investigated. The response of additions of cadmium(II) using an EPPG electrode in a 0.1 M acetate buffer solution pH 4.5 containing 1 mg/L Bi(III) was explored. The stripping voltammograms from additions of cadmium(II) over the range of 0.1 to 150 µg/L are investigated, where the peak height *versus* added concentration of cadmium(II) was found to produce two linear ranges. The first range of cadmium(II) calibration curve was linear between 0.1 to 10 µg/L ($I_H(A) = 6.74 \times 10^{-8}[Cd(\mu g/L)]$ + $6.24 \times 10^{-9}A$; $N = 7$, $R^2 = 0.99$) and the second range of calibration curve was linear from 10 to 150 µg/L ($I_H(A) = 1.8 \times 10^{-7}[Cd(\mu g/L)] - 1.56 \times 10^{-6}C$; $N = 7$, $R^2 = 0.99$). A detection limit of 0.079 µg/L (based on 3σ) was found for cadmium(II) using this plot.

Next the additions of cadmium(II) in the presence of 30 µg/L lead(II) was explored, where two linear ranges obtained over the range of 0.1 – 200 µg/L for cadmium(II) which is shown in Fig. 3. The first range of calibration curve was linear from 0.1 to 20

Table 2   Methods with lowest detection limits reported for determination of cadmium(II) and lead(II) using mercury based electrodes

| Electrode	Modifier	Method	LOD of Cd/µg L^{-1}	LOD of Pb/µg L^{-1}	Ref.
GCE	Hg film	DPASV	0.0001	—	50
Glassy carbon disk	Hg film-thiocyanate	ASV	≈0.00056	≈0.0016	51
Rotating GCE	Hg film	PSA	0.001	0.003	52
Carbon fibre-Pt	Hg film	ASV	≈0.0013	NA	53
Mercury	—	CSV and ASV	≈0.0018	≈0.0041	54
GCE	Modified Hg film	ASV	≈0.0034	≈0.0062	55
Hg film	—	PSA	≈0.005	≈0.005	56
HMDE	—	ASPP	≈0.0056	NA	57
BDD-HMDE	—	SonoASV	≈0.005	≈0.07	58
HMDE	APSH	DPAdsCSV	0.0067	—	59
Iridium based nanoelectrode	Hg film	SWASV	≈0.0056	≈0.01	60
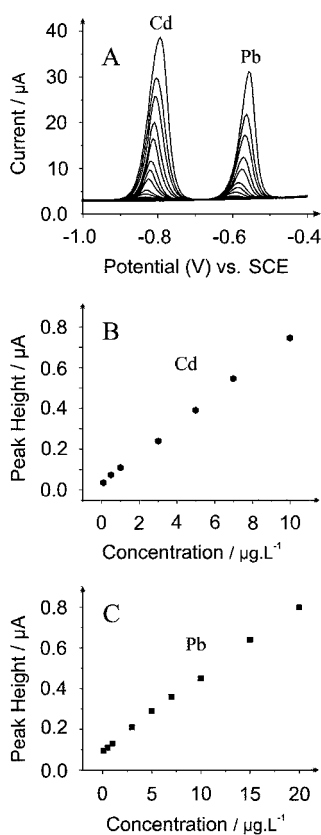
Fig. 5 (A) Anodic stripping voltammograms for simultaneous additions of 0.1, 0.5, 1, 3, 5, 7, 10, 15, 20, 30, 40, 50, 75, 100, 150, 200 and 300 µg/L Cd(II) and Pb(II) on EPPG electrode in 0.1 M acetate buffer pH 4.5 in the presence of 1 mg/L Bi(III). (B) First linear range of calibration curve of Cd(II) in simultaneous additions of Cd(II) and Pb(II). (C) First linear range of calibration curve of Pb(II) in simultaneous additions of Cd(II) and Pb(II).

µg/L ($I_{\mathrm{H}}(A) = 9.67 \times 10^{-8}$[Cd(µg/L)] $- 5.39 \times 10^{-9}A$; $N = 9$, $R^2 = 0.99$) and the second range of calibration curve was linear from 20 to 200 µg/L ($I_{\mathrm{H}}(A) = 1.98 \times 10^{-7}$[Cd(µg/L)] $- 2.09 \times 10^{-6}A$; $N = 8$, $R^2 = 0.99$). The stripping voltammograms of second linear range of cadmium(II) additions in the presence of 30 µg/L lead(II) are shown in Fig. 3A, and the voltammograms and related calibration curve for the first linear range of cadmium(II) additions in the presence of 30 µg/L lead(II) are shown in Figs. 3B and 3C, respectively. A detection limit of 0.081 µg/L (based on 3σ) was obtained using this curve.

Additions of lead(II) in the presence of 40 µg/L cadmium(II) were also explored and two linear ranges were achieved between 0.2 and 200 µg/L. The first range of this calibration curve is linear from 0.2 to 30 µg/L ($I_{\mathrm{H}}(A) = 5.71 \times 10^{-8}$[Pb(µg/L)] $+ 8.99 \times 10^{-8}A$; $N = 9$, $R^2 = 0.99$) and the second range of calibration curve is linear from 30 to 200 µg/L ($I_{\mathrm{H}}(A) = 9.31 \times 10^{-8}$[Pb(µg/L)] $- 1.02 \times 10^{-6}A$; $N = 7$, $R^2 = 0.99$). Figure 4A shows the voltammograms for the second range of calibration curve while Figs. 4B and 4C show the voltammograms and related calibration curve for the first linear range of lead(II) additions in the presence of 40 µg/L cadmium(II), respectively, where a detection limit (based on 3σ) of 0.101 µg/L is obtained from this curve.

Finally we explored the simultaneous additions of cadmium(II) and lead(II) in optimized conditions which showed two well-defined and highly resolved peaks in potentials of ≈−0.84 V and ≈−0.59 V which are shown in Fig. 5A. These additions produced two linear ranges for cadmium(II) and lead(II). The first calibration range of cadmium(II) (Fig. 5B) is linear from 0.1 to 10 µg/L ($I_{\mathrm{H}}(A) = 7.17 \times 10^{-8}$[Cd(µg/L)] $+ 3.37 \times 10^{-8}A$; $N = 7$, $R^2 = 0.99$) and the second calibration range of cadmium(II) (not shown) is linear from 10 to 100 µg/L ($I_{\mathrm{H}}(A) = 1.97 \times 10^{-7}$[Cd(µg/L)] $- 1.48 \times 10^{-6}A$; $N = 8$, $R^2 = 0.99$) while the first calibration range of lead(II) (Fig. 5C) is linear from 0.1 to 20 µg/L ($I_{\mathrm{H}}(A) = 3.54 \times 10^{-8}$[Pb(µg/L)] $+ 9.97 \times 10^{-8}A$; $N = 9$, $R^2 = 0.99$) and the second linear range (not shown) is from 20 to 300 µg/L ($I_{\mathrm{H}}(A) = 9.74 \times 10^{-8}$[Cd(µg/L)] $- 1.04 \times 10^{-6}A$; $N = 9$, $R^2 = 0.99$).

Figures 5B and 5C depict the first range of calibration curves for cadmium(II) and lead(II); using these first linear ranges of calibration curves, detection limits (based on 3σ) of 0.062 and 0.084 µg/L are obtained for cadmium(II) and lead(II), respectively.

As mentioned before, mercury based electrodes are the most sensitive electrodes for the determination of heavy metals using voltammetric techniques; the best detection limits for the determination of lead(II) and cadmium(II) using mercury based electrodes are listed in Table 2. The lowest detection limits for the determination of lead(II) and cadmium(II) using non-mercury based electrodes are listed in Table 3. With comparing the detection limits in Tables 2 and 3, it is evident that mercury based electrodes are much more sensitive than non-mercury based ones for cadmium(II) and lead(II) detection. But toxicity of these mercury based electrodes make them unfavored electrode materials. The detection limit of cadmium(II) and lead(II) using our proposed BiF-EPPGE is the same order of magnitude as the lowest detection limits using non-mercury based electrodes including bismuth film modified carbon nanotube nanoelectrode array[14] and our proposed BiF-EPPGE is also superior to all of previous bismuth modified electrodes (see

Table 3 The methods with lowest detection limits reported for determination of cadmium(II) and lead(II) using non-mercury based electrodes

Electrode	Modifier	Method	LOD of Cd/μg L⁻¹	LOD of Pb/μg L⁻¹	Ref.
GCE	Nafion film	Voltammetry	0.0056	—	61
Gold UME	—	FSCV	≈0.07	≈0.06	45
GCE	Heparin	DPASV	—	≈0.062	62
CPE	Zr-Ph silica	DPASV	—	≈0.0725	47
Gold	—	SWSV	—	0.08	63
CPE	BHAMS	DPASV	—	≈0.081	48
BDD	—	SonoSV	≈0.112	—	46

GCE, Glassy carbon electrode; DPASV, differential pulse anodic stripping voltammetry; PSA, potentiometric stripping analysis; CSV, cathodic stripping voltammetry; ASPP, anodic stripping pulse polarography; HMDE, hanging mercury drop electrode; BDD, boron doped diamond; SonoASV, ultrasound assisted anodic stripping voltammetry; DPAdsCSV, differential pulse adsorptive cathodic stripping voltammetry; APSH, 2-acetylpyridine salicyloylhydrazone; Gold UME, gold ultra micro electrode; FSCV, fast stripping cyclic voltammetry; SWSV, square wave stripping voltammetry; CPE, carbon past electrode; BHAMS, bis(1-hydroxy-9,10-anthraquinone-2-methyl)sulphide; Zr-Ph silica, zirconium phosphated silica.

Table 1).   The large number of nucleation sites for the deposition of bismuth, *viz*. edge plane sites are likely responsible.   It is worth mentioning that some of the non-mercury based electrodes used for the detection of cadmium(II) and lead(II), as detailed in Table 3, suffer from complexity in manufacturing the electrodes,[14] instrumentation[45,46] and/or modification process or synthesis of modifiers such as complexing agents.[47,48]   Compared to these requirements, the handling of our proposed electrode is much more simple and can be easily used in every electrochemical lab.

Analysis of real sample

  The proposed protocol based on using bismuth film modified EPPG electrode was then utilised for the simultaneous determination of cadmium(II) and lead(II) in a spiked sample of Cherwell river (Oxford) as a "real" sample.   A solution of the river water was diluted in a ratio of 1:5 with acetate buffer solution pH 4.5 which was spiked with 1 μg/L cadmium(II) and 1 μg/L lead(II).   Additions of cadmium(II) and lead(II) were then made to the solution.   The response of additions is shown in Fig. 6A, where analysis of the peak height *versus* added cadmium(II) and lead(II) concentration is shown in Figs. 6B and 6C, respectively.   Based on this recovery experiment, 1.05 and 0.98 μg/L was determined for cadmium(II) and lead(II) from the standard addition plot resulting recoveries of 100.5 and 98% for cadmium(II) and lead(II), respectively.   Clearly this electrode may be utilised for simultaneous determination of cadmium(II) and lead(II) in real samples.

Fig. 6 (A) Anodic stripping voltammograms for simultaneous additions 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 μg/L of Cd(II) and Pb(II) on EPPG electrode in bufferized real sample (Cherwell river water) in the presence of 1 mg/L Bi(III).   The dotted line shows the blank signal of EPPGE in real sample before spiking Cd(II) and Pb(II).   The dashed-dotted line shows the signal of real sample after spiking 1 μg/L Cd(II) and 1 μg/L Pb(II), and solid lines show the additions of Cd(II) and Pb(II) from 1 to 10 μg/L.   (B) and (C) are the same as in Figs. 5(B) and (C), respectively.

be used for the routine analysis of cadmium(II) and lead(II) in different real samples.   We note that the beneficial use of edge plane pyrolytic graphite with its large number of edge plane sites facilitates the nucleation of bismuth thus providing one of the simplest electroanalytical methods using non-mercury based electrodes for simultaneous determination of cadmium(II) and lead(II) to date.

Conclusions

An edge plane pyrolytic graphite electrode was modified with an *in-situ* electro-deposition of bismuth film and was then successfully utilised for the simultaneous determination of cadmium(II) and lead(II) in standard and real samples.   This method with the aid of the BiF-EPPG electrode has advantages such as low detection limit, wide linear dynamic range, easy handling and modification, mercury free and low cost which can
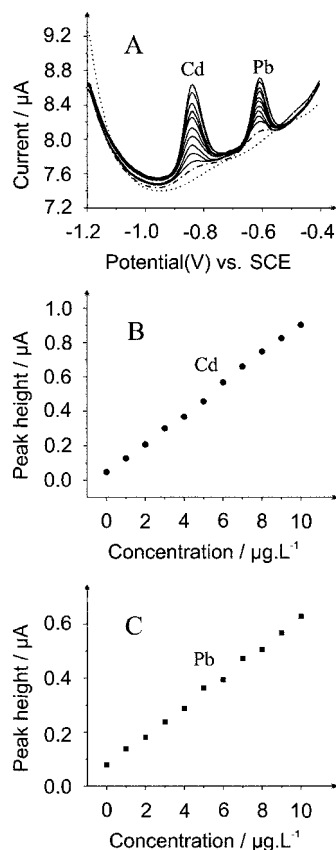
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