

Analytical Methods

A Nafion-coated bismuth film electrode for the determination of heavy metals in vegetable using differential pulse anodic stripping voltammetry: An alternative to mercury-based electrodes

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Abstract

Mercury electrodes have been traditionally employed for achieving high reproducibility and sensitivity of the stripping technique. However, new alternative electrode materials are highly desired because of the toxicity of mercury. Bismuth is an electrode material characterized by its low toxicity and its ability to form alloys with some metals such as cadmium, lead and zinc, allowing their preconcentration at the electrode surface. In this work, we reported the simultaneous determination of Pb(II), Cd(II) and Zn(II) at the low $\mu\text{g/l}$ concentration levels by differential pulse anodic stripping voltammetry (DPASV) on a Nafion-coated bismuth film electrode (NCBFE) plated in situ, and investigated the application of NCBFE to heavy metals analysis in vegetable samples. The analytical performance of NCBFE was evaluated for simultaneous determination of Pb(II), Cd(II) and Zn(II) in non-deaerated solution, with the limits of determination of 0.30 $\mu\text{g/l}$ for Zn, 0.17 $\mu\text{g/l}$ for Cd and Pb at a preconcentration time of 180 s. High reproducibility for NCBFE was indicated from the relative standard deviations of 2.4% for Pb, 2.0% for Cd and 3.4% for Zn at the 15 $\mu\text{g/l}$ level ($n = 15$). The NCBFE was successfully applied to determine Pb and Cd in vegetable samples, and the results were in agreement with those of graphite furnace atomic absorption spectrometry (GFAAS).

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Keywords: Nafion-coated bismuth film electrode; Anodic stripping voltammetry; Heavy metals

1. Introduction

Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment, since they have a significant effect on ecological quality. Toxic and persistent substances in the environment continuously increase owing to anthropic activities. In particular, the rapid diffusion of heavy metals as environmental contaminants has necessitated their determination at trace and ultra trace levels. In fact, such elements tend to concentrate in all matrices involved in foods and food chains because of their irreversible deleterious effects on man (Merian, 1991; Muñoz-Olivas & Cámara, 2001).

Therefore, great attention must be addressed to everything directly concerning the human healthy, especially diet and nutrition. As well-known, trace elements play a very important role in human nutrition. Their quantities in the human body vary so much that in many instances they are essential to life, while in others they are toxic even at very low concentrations. Vegetable are part of the human diet all over the world, so it is very important to determine the heavy metals in vegetable.

Different techniques and methods have been developed for trace metals determination. Using electrothermal atomic absorption spectrometry (ETAAS), Cd and Pb in food have been analyzed (Alexiu & Vladescu, 2003; Falomir, Alegria, Barbera, Farre, & Lagarda, 1999). Neutron activation techniques have high sensitivity for trace metals, but they are not used frequently because of the specialized techniques, long

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time and high cost involved (Yanaga, Iwama, Takiguchi, Noguchi, & Omori, 1998). Other techniques such as atomic emission spectrometry with inductively coupled plasma excitation (AES-ICP) (Hennebrüder, Wennrich, Mattusch, Stark, & Engewald, 2004) and X-ray fluorescence (XRF) (Stosnach, 2006) are very expensive and do not offer sufficient sensitivity for accurate determination of trace elements. Electrochemical stripping analysis has long been recognized as a powerful technique for trace metals owing to its remarkable sensitivity, relatively inexpensive instrumentation, ability for multi-element determination and capable of determining elements accurately at trace and ultra trace levels (Achterberg & Braungard, 1999; Batley, 1983; Wang, 1985).

Mercury film electrode (MFE) and the hanging mercury drop electrode (HMDE) have been traditionally used for ASV owing to the advantageous analytical properties of mercury in the negative potential range. However, because of the toxicity of mercury, future regulations and occupational health considerations may severely restrict (or ban) the use of mercury as an electrode material (Wang, 2002). New alternative electrode materials are highly desired to develop 'environmentally friendly' stripping sensors for meeting the growing demands for on-site environmental monitoring of trace metals. Since the year 2000, bismuth film electrodes (BFEs) have become an attractive new subject of electroanalytical investigations as a potential replacement for mercury and mercury film electrodes (Economou, 2005; Wang, 2005; Wang, Lu, Hocevar, Farias, & Ogorevc, 2000). The behavior of bismuth electrodes has been shown to compare favorably to that of mercury electrodes, with attractive properties such as high sensitivity, well-defined stripping signals, good resolution of neighbouring peaks, wide cathodic potential range, and insensitivity to dissolved oxygen. This latter characteristic is an essential property for on-site monitoring. The advantageous properties of bismuth are attributed to its ability to form "fused" or "low-temperature" alloys with heavy metals (Krueger, Winkler, Luederitz, & Lueck, 1985; Long, Freeman, & Doak, 1978), facilitating the nucleation process during accumulation of heavy metal ions and leading to almost the sensitivity of mercury film electrodes. In addition, bismuth is a more 'environmentally friendly' material with a low toxicity and widely used in the pharmaceutical and cosmetic industry.

Most of the earlier work on BFEs was concerned with insights into their fundamental properties. However, its application to environment, clinical, and food analysis was still rather limited and immature (Economou, 2005). In this article, we performed a thorough study of the parameters affecting the electrochemical behavior of NCBFE to achieve high sensitivity for simultaneous determination of Pb(II), Cd(II) and Zn(II) in real samples. The most appropriate conditions were used for analytical application of ASV on a NCBFE, namely the determination of Pb(II), Cd(II) and Zn(II) in vegetable samples.

2. Experimental section

2.1. Apparatus

Differential pulse stripping voltammetry was performed with a CHI660A electrochemical workstation (Chenhua Instrumental Corporation, Shanghai), in connection with a personal computer. A Nafion-coated glassy carbon (GC) disk (3 mm diameter, BAS) served as working electrode, with the Ag/AgCl (3 mol l⁻¹ NaCl) and platinum wire acting as reference electrode and counter electrode, respectively. All glassware was carefully cleaned by soaking in 0.1 mol l⁻¹ HNO₃ over 48 h, followed by thorough rinsing with copious amounts of ultrapure water. Stirring was carried out using a magnetic stirrer. Graphite furnace atomic absorption spectrometry (Solaar M₆, Thermo Elemental, USA) was used as a reference method. No deaeration of the solutions was applied at any stages of this study. All potentials were given versus the Ag/AgCl (3 mol l⁻¹ NaCl) electrode.

2.2. Reagents

All the chemicals were of analytical grade. Nafion (5% w/v solution in a mixture of water and lower aliphatic alcohols) was purchased from Aldrich. The dilute Nafion solutions were prepared with absolute ethanol. The bismuth, lead, cadmium, zinc and mercury were prepared from 1000 mg/l atomic absorption standard solutions after appropriate dilution with 1% (Cd, Zn and Pb) or 5% (Bi, Hg) nitric acid (w/v). An acetate buffer solution (0.1 mol l⁻¹, pH 4.5) served as the supporting electrolyte. Stock solutions (500 mg/l) of sodium dodecyl sulfate, gelatin, tetrabutylammonium bromide (Sinopharm Chemical Reagent Co. Ltd, China), Triton X-100 (Aldrich) were used as surface-active compounds.

2.3. Sample preparation

Each representative sample of vegetable was purchased from local supermarket. The vegetable samples were washed with deionized water thoroughly and dried at 60 °C for 12 h, then they were accurately weighed in a 50 ml quartz crucible (approximately 1 g). The sample was completely carbonized on a hot plate, then transferred in a muffle oven and the temperature was slowly increased up to 500 °C. The sample was dry-ashed until white ashes were obtained totally. The ashes were dissolved with concentrated nitric acid and perchloride acid (4:1), gently heating on a hot plate until almost dry. Then the solution was cooled at room temperature and quantitatively transferred to a 25 ml volumetric flask with 0.5% nitric acid. The sample treatment was used for the preparation of five blanks and of the samples for GFAAS determination.

2.4. Procedure

The glassy carbon electrode was polished with water slurry of 0.05 µm Al₂O₃, rinsed with ethanol and water

and dried. A 5 μl drop of the Nafion solution was placed on the surface of the glassy carbon electrode with a micropipette and solvents were left to evaporate at room temperature for 10 min. Then the film was treated with a jet of warm air for about 1 min and left to cool at room temperature before being used. This heat treatment has been shown to improve the stability of the Nafion membrane (Hoyer & Jensen, 1994).

The electrochemical deposition of bismuth and the other metals on the bare glassy carbon electrode (GCE) or Nafion-coated GCE was done according to an in situ procedure in the presence of dissolved oxygen. The three electrodes were immersed into a 10 ml electrochemical cell, containing 0.1 mol l^{-1} acetate buffer (pH 4.5) and appropriate bismuth. The deposition potential was applied to the bare GCE or Nafion-coated GCE, while the solution was stirred. Following the preconcentration step (usually 180 s), the stirring was stopped. After 10 s, differential pulse voltammetry was performed by potential scan from -1.4 V to 0.0 V with amplitude of 50 mV , pulse width of 50 ms and potential step of 4 mV . Aliquots of the target metal standard solution were introduced after the background signal was recorded. Prior to the next cycle, a 30 s conditioning step at $+0.3 \text{ V}$ (with solution stirring) was used to remove the target metals and bismuth. In situ plated Nafion-coated mercury film electrode (NCMFE, $1000 \mu\text{g/l}$ mercury) was used under the similar measurement procedures. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Electrochemical responses of bare GCE, BFE and NCBFE

Fig. 1 shows the stripping performance of $25 \mu\text{g/l}$ Pb(II), Cd(II) and Zn(II) at bare GCE, BFE and NCBFE. As seen in Fig. 1, very small and distorted stripping peaks of Pb and Cd were observed at the bare GCE and the signal of Zn was not obtained (Fig. 1a). When $400 \mu\text{g/l}$ bismuth was added to the sample, and electrodeposited along with the target metals simultaneously, distinct and undistorted stripping peaks for analytes were achieved (Fig. 1b). Moreover, the stripping signals of target metals at NCBFE were more remarkable and attractive (Fig. 1c). Compared with BFE, the electrochemical signals on NCBFE were improved about 35% for Pb, 46% for Cd and 46% for Zn. This phenomenon can be attributed to the cation ion-exchange property of Nafion film. At pH 4.5, the sulfonate groups in the Nafion film are negatively charged and, as a result, the polymeric membrane acts as a cation-exchanger and facilitates the non-faradaic preconcentration of metal cations (Agra-Gutiérrez, Suares, & Compton, 1999; Dam & Schroeder, 1996). Therefore, the presence of the Nafion film may account for the improvement in sensitivity on the NCBFE. Compared with the bare BFE, the peak potentials of the three metals on the

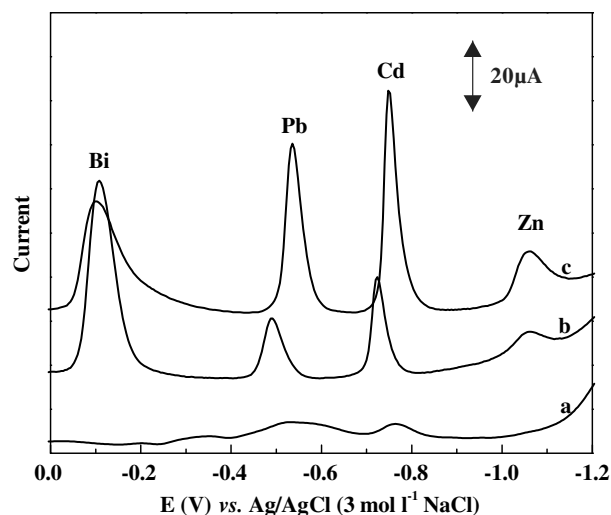


Fig. 1. Differential pulse stripping voltammograms of $25 \mu\text{g/l}$ Pb(II), Cd(II) and Zn(II) at bare GCE (a), bare GCE with $400 \mu\text{g/l}$ bismuth (b) and Nafion-coated GCE with $1000 \mu\text{g/l}$ bismuth (c) in 0.1 mol l^{-1} acetate buffer (pH 4.5). Deposition for 180 s at -1.4 V ; “cleaning” for 30 s at $+0.3 \text{ V}$; differential pulse voltammetric stripping scan with an amplitude of 50 mV , pulse width of 50 ms and potential step of 4 mV .

NCBFE were also shifted to the cathodic direction, indicating the coulombic interactions between the cation-exchanging Nafion film and the accumulated metals.

3.2. Comparison the stripping performance between NCBFE and NCMFE

Fig. 2 displays the typical anodic stripping voltammograms for $25 \mu\text{g/l}$ Pb(II), Cd(II) and Zn(II) at NCMFE (a) and NCBFE (b). Well-defined, sharp and separated peaks were observed after the 180 s deposition at both electrodes. However, the stripping signals of Cd and Pb on the

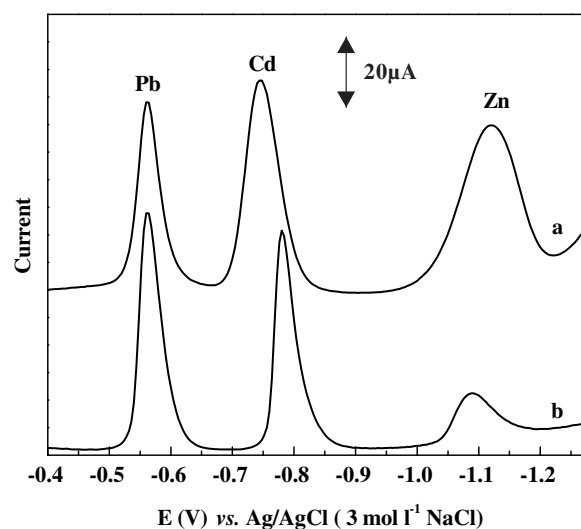


Fig. 2. Differential pulse stripping voltammograms of $25 \mu\text{g/l}$ Pb(II), Cd(II) and Zn(II) at in situ plated NCMFE (a) and NCBFE (b). Conditions as in Fig. 1.

NCBFE were obviously enhanced (15% for Pb and 8% for Cd), while the sensitivity for Zn was worse compared to NCMFE. The potentials of Pb and Zn peaks were approximately the same on the two electrodes, but the Cd peak on the NCBFE was shift to more negative values. Hence, the resolution between the Cd and Pb peaks was improved on the NCBFE. In addition, the peak at the NCBFE was sharper than that at NCMFE with the peak half widths of 39 mV for Pb and 34 mV for Cd. The peak half widths of Pb and Cd at NCMFE were 41 mV and 62 mV, respectively. The differential pulse scan resulted in a low (nearly flat) background current in the presence of dissolved oxygen, and the signal-to-noise was not compromised by the use of the bismuth coating instead of the mercury film.

3.3. Effect of the concentration of bismuth ion

The influence of the bismuth ion concentration on the peak currents of Pb and Cd was studied in the range 200–2000 µg/l for a solution containing 25 µg/l Pb(II), Cd(II) and Zn(II) in 0.1 mol l⁻¹ acetate buffer (pH 4.5) at in situ plated NCBFE. The concentration of the Bi(III) ion controlled the thickness of the Bi film, whereas the thickness of the film did not affect the peak position of any metals. For Bi(III) concentrations lower than 1000 µg/l, the height of the Pb and Cd peaks were slightly affected by the Bi(III) concentrations, and the height of the Zn peak increased with increasing concentrations of Bi(III) ion. However, for Bi(III) concentrations higher than 1000 µg/l, the Pb, Cd and Zn peaks decreased with increasing bismuth film thickness. It also indicated that the background current at negative potentials, where the Zn peak appeared, increased with the amount of Bi deposited; this resulted in a more sloping baseline for Zn peak. The results revealed that the best combination of sensitivity, peak sharpness and background current (especially close to the Zn peak) was obtained for Bi(III) concentration of 1000 µg/l.

3.4. Effect of the concentration of Nafion

The Nafion concentration has a profound effect on the stripping response. All the Nafion-coated electrodes exhibited higher sensitivity than bare BFE. In addition, we found that the peak current was higher for 1% Nafion compare to that of 0.5%, 1.5% and 2% Nafion. Indeed, at very thin or very thick polymer films, the stripped species were able to diffuse away from electrode due to incomplete coating or cracks, respectively (Hoyer, Florence, & Batley, 1987). In view of these results, the 1% Nafion solution was selected for further work.

3.5. Effect of the preconcentration time

The metal preconcentration time was studied in the range 40–600 s for a solution containing 25 µg/l each of Pb(II), Cd(II) and Zn(II) in 0.1 mol l⁻¹ acetate buffer (pH

4.5) at in situ plated NCBFE. The peak heights increased linearly up to 420 s, while at higher deposition time the peak heights versus time plots started to deviate from linearity. In this work, 180 s was selected as the preconcentration time.

3.6. Tolerance to surface-active compounds

The surfaces of solid electrodes, such as glass carbon, tend to be blocked over time when they are employed in analyses in natural media due to irreversible adsorption of electroactive and other chemical species. It might lead to lower or broader peaks, shifts in the peak potential and the decrease of response in the analysis of natural media (Sagberg & Lund, 1982). Such surface fouling is the main limitation of direct ASV measurements in complex environmental, clinical or food samples. The surfactant problem can be minimized through coverage with a permselective/protective film. Nafion, as ion-exchanger polymer, nonelectroactive, hydrophilic and insoluble in water possesses ideal properties for preparation of modified electrodes, which represents sufficiently good discrimination against potential adsorbents and interfering species for application to natural media (Hoyer et al., 1987).

BFEs and MFEs were prone to interference from surface-active compounds that adsorbed on the electrode and caused deactivation of its surface (Wang, Deo, Thongngamadee, & Dgorevc, 2001; Wang & Luo, 1984). For this work, Triton X-100 and gelatin (non-ionic surfactants), sodium dodecyl sulfate (anionic surfactant) and tetrabutylammonium bromide (cationic surfactant) were selected as “model” surfactant compounds. The effect of these surface-active compounds was studied at the NCBFE (1% Nafion) and the BFE under identical conditions, which was shown in Fig. 3A and B. The Zn(II) peak was the most severely affected by the presence of surfactants and it was completely suppressed on the BFE (Fig. 3A). However, the Nafion-modified BFE exhibited better tolerance to the presence of surfactants than that the bare BFE as the reduction in peak heights was less severe than that on the bare BFE with the Zn(II) peak well-defined in all cases (Fig. 3B). This resistance to surfactants was attributed to the effective barrier layer of polymeric film for preventing the transport of macromolecules to the electrode surface.

The stability of NCBFE was tested by carrying out the continuous operation ca 80 min in the solution containing 25 µg/l of Pb(II), Cd(II), Zn(II) and 10 mg/l gelatin. Between the 1st and the 20th measurements, the drift in the peak height of Pb(II), Cd(II) and Zn(II) were 8%, 5% and 12%, indicating that a satisfactory stability of the sensor.

3.7. Calibration data

A series of stripping voltammograms for Pb(II), Cd(II) and Zn(II) at concentration range 4–36 µg/l is described in Fig. 4. The correlation coefficients were 0.9975, 0.9985

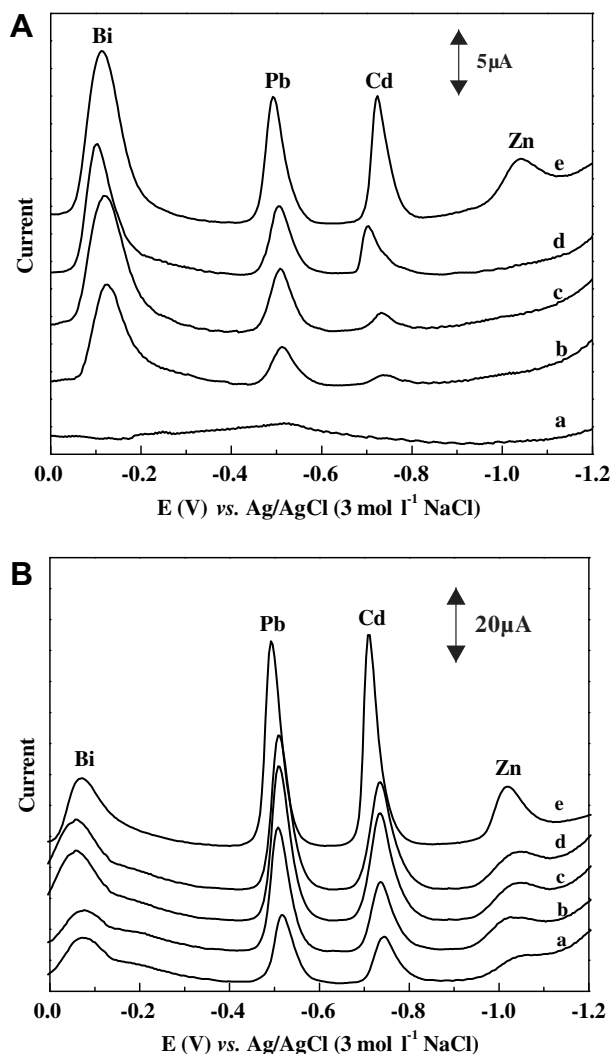


Fig. 3. Effect of 10 mg/l (a) Triton X-100, (b) sodium dodecyl sulfate, (c) gelatin, and (d) tetrabutylammonium bromide on the ASV response of a solution containing 25 µg/l of Pb(II), Cd(II) and Zn(II) at (A) BFE and (B) NCBFE. Traces (e) are the responses in the absence of surfactants. Conditions as in Fig. 1.

and 0.9964 for Pb(II), Cd(II) and Zn(II), respectively. The relative standard deviations were 2.4% for Pb, 2.0% for Cd and 3.4% for Zn at the 15 µg/l level ($n = 15$) with preconcentration time of 180 s. The limits of determination were 0.30 µg/l for Zn, 0.17 µg/l for Pb and Cd with deposition time of 180 s.

3.8. Determination of lead, cadmium and zinc in the vegetables sample

One milliliter of sample solution was adjusted to pH 4.5 with NaOH and diluted to 5 ml with 0.1 mol l⁻¹ acetate buffer (pH 4.5), then was placed in the cell without deaeration. Stripping voltammetric measurements were performed with an in situ deposition of the bismuth and target metals (e.g. Pb, Cd and Zn), and deposition was carried out for 180 s at -1.4 V, while the solution was stirred.

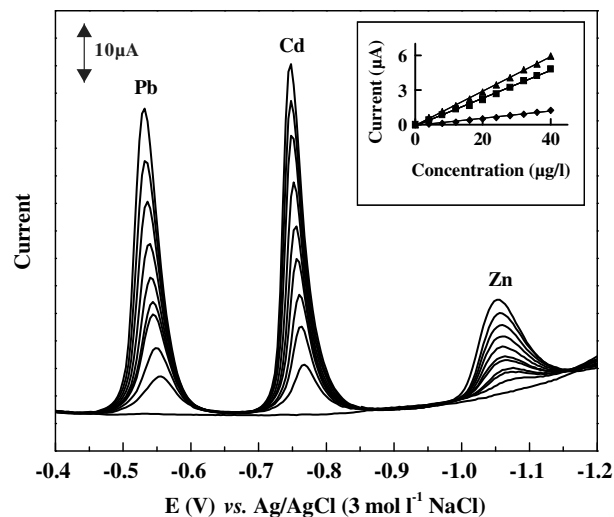


Fig. 4. A series of voltammograms for increasing concentrations of Pb(II), Cd(II) and Zn(II) on an in situ plated NCBFE (Pb: ■; Cd: ▲; Zn: ◆). From below: blank and successive additions of 4 µg/l of Pb(II), Cd(II) and Zn(II). Conditions as in Fig. 1.

After the solution was left in quiescence for 10 s, differential pulse stripping voltammogram of the solution was recorded by scanning the potential toward the positive direction. Fig. 5 is the stripping voltammograms for the determination of Pb, Cd and Zn in the cabbage sample. It was evident that the well-defined Pb and Cd peaks were obtained. Standard addition of 5 µg/l Pb and Cd caused an increment at the sample potential and made the determination of Pb and Cd in the cabbage sample possible. Although a well-defined Zn peak was also obtained in cabbage sample, the quantification of Zn was unsuccessful due to the formation of a well-known intermetallic compound with native Cu(II) in the sample, a complication that can

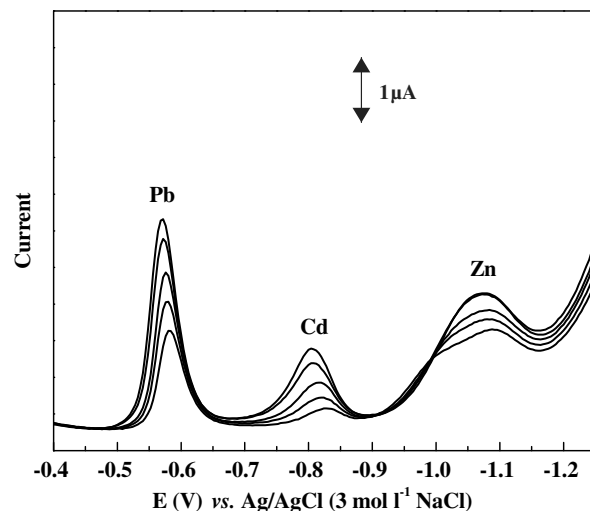


Fig. 5. DPASV signals for the determination of Pb(II), Cd(II) and Zn(II) in the cabbage sample on in situ plated NCBFE. From below: sample and successive standard additions of 5 µg/l Pb and Cd and 10 µg/l Zn. Conditions as in Fig. 1.

Table 1
Results for the determination of Pb and Cd in five vegetables sample by DPASV and GFAAS

Vegetables sample	DPASV ⁿ (μg/l)		GFAAS ⁿ (μg/l)	
	Pb	Cd	Pb	Cd
Cabbage	2.20 ± 0.02	1.57 ± 0.02	2.19 ± 0.01	1.58 ± 0.02
Lettuce	4.85 ± 0.02	3.50 ± 0.04	4.89 ± 0.03	3.60 ± 0.03
Celery ₁	1.20 ± 0.03	2.12 ± 0.04	1.18 ± 0.05	2.08 ± 0.03
Spinage	1.28 ± 0.05	1.05 ± 0.09	1.30 ± 0.08	1.06 ± 0.06
Celery ₂	4.17 ± 0.04	1.52 ± 0.02	4.20 ± 0.05	1.54 ± 0.03

n: number of experiments (*n* = 4). Celery₁ and celery₂ were collected from different areas.

be alleviated with the addition of Ga(III) ions in the sample, because Ga(III) preferentially bound Cu and released Zn. However, the concentration of Cu(II) in the sample was unknown. If amount of Ga(III) added was not enough, it would incompletely bind Cu and Zn would not be released totally. When the amount largely exceeded the content of Cu(II), Ga(III) would interfere with the quantification of Zn (Wang, Lu, Kirgoz, Hocevar, & Ogorevc, 2001). Therefore, we investigated the determination of Pb and Cd in vegetable samples by ASV with NCBFE. The same determinations were also carried out by GFAAS which was used as a reference method. The experimental results, shown in Table 1, suggested that there was a satisfactory agreement between the two techniques.

4. Conclusion

In this study, we developed a novel method to determine heavy metals in vegetable samples by differential pulse anodic stripping voltammetry on a Nafion-coated bismuth film electrode plated in situ. The selectivity of this electrode for simultaneous analysis of heavy metals in natural media open the possibility to consider the Nafion-coated bismuth film electrode as a good alternative to mercury-based electrodes. It has also been demonstrated that permselective Nafion film on the NCBFE can significantly improve sensitivity, tolerance to surfactants and long-term stability of the electrode. NCBFE was successfully applied to the determination of Pb and Cd in vegetable, and the results were in satisfactory agreement with GFAAS determination. Owing to the low toxicity of bismuth, inexpensive instrumentations, and simple operation, the methods will offer potential applications for on-site monitoring of heavy metals in environment, food and medicine.

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