Nafion-Coated Bismuth Film Electrodes for the Determination of Trace Lead and Cadmium in Herbal Medicines by Anodic Stripping Voltammetry

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A novel analytical procedure for the determination of Pb(II) and Cd(II) in herbal medicines by differential pulse anodic stripping voltammetry (DPASV) on Nafion-coated bismuth film electrode (NCBFE) was proposed and experimentally validated. Various experimental parameters, which influenced the response of the NCBFE to these metals in real samples, were optimized. The results showed that there were well-defined peaks of Pb and Cd in herb samples at deposition potential of -1.2 V and deposition time of 300 s. The analytical performance of the NCBFE was evaluated in the presence of dissolved oxygen, with the determination limits of 0.35 μ g•L⁻¹ for Pb and 0.72 μ g•L⁻¹ for Cd and recoveries of 87.8%—105.4% for Pb and 89.5%—108.5% for Cd obtained from different samples. The Pb and Cd concentrations in the studied samples have been also determined by graphite furnace atomic absorption spectrometry (GFAAS), suggesting that there was a satisfactory agreement between the two techniques, with relative errors lower than 6.5% in all cases. The great advantages of the proposed method over the spectroscopic method were characterized by its simplicity, selectivity and short analysis time, simultaneous analysis of different metals and cost-efficiency.

Keywords nafion-coated bismuth film electrode, stripping voltammetry, herbal medicine, heavy metal

Introduction

Herbal medicine is one form of complementary and alternative medicine widely used by people all over the world. The World Health Organization estimates that 65% to 80% of the world's population use traditional medicine as their primary form of healthcare.^{1,2} Herbal teas and herbal extracts are considered to be effective drugs of curing diseases and to have few side-effects on many people who are also prescribing them as supplementary type of treatment in everyday problems caused by our modern civilization.³ Although herbal remedies are perceived as being natural and safe, they are not free from adverse effects. One of the major problems in herbal medicine is related to heavy metals caused serious health hazards.⁴ Chronic exposure to cadmium can cause nephrotoxicity in humans, mainly due to abnormalities of tubular re-absorption.⁵ Lead can cause adverse effects on the renal and nervous systems and can cross the placental barrier, with potential toxic effects on the fetus.⁶

Most of literatures described the use of spectroscopy as the instrumental techniques for determination of trace metals in herbal medicines.⁷⁻⁹ Few studies regarding the determination of toxic metals in herbal medicines, especially for cadmium and lead, were proposed by electrochemical methods. Electrochemical stripping analysis has long been recognized as a powerful technique for measuring trace metals. It possesses some intrinsic advantageous features such as high sensitivity due to the built-in preconcentration step, selectivity, inexpensive and portable instrumentations, and the ability to determine multi-element accurately at trace and ultra-trace levels.¹⁰

Mercury film electrode (MFE) and the hanging mercury drop electrode (HMDE) have been traditionally used for anodic stripping voltammetry (ASV) owing to their high reproducibility and sensitivity. 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.¹¹ 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 electrode (BFE) has been attracting increasing attention in the field of electrochemical stripping analysis,¹²⁻¹⁴ as an alternative and possible replacement for mercury-based electrodes. The performance of bismuth electrodes have been proven to compare favorably to or even surpass that of mercury electrodes, with attractive properties such as high sensitivity, well-defined

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stripping signals, excellent peak resolution , relatively large negative potential range, and insensitivity to dissolved oxygen.¹⁵ This latter characteristic was an essential property for on-site monitoring. In addition, bismuth was an environmentally friendly, non-toxic "green" material and widely used in the pharmaceutical and cosmetic industry.¹⁶ Most of the earlier work on Nafioncoated bismuth film electrode (NCBFE) was concerned with insights into their fundamental properties.¹⁷ However, its applications to environmental and herbal analyses were still rather limited and immature.

In this work, we developed Nafion-coated bismuth film electrodes to determine Pb(II) and Cd(II) in herbal medicines commercially available in China by differential pulse anodic stripping voltammetry. The performance of the NCBFE was studied for stripping signals, recoveries and determination limits of Pb and Cd in herb samples. The results showed that the NCBFE had high sensitivity, good selectivity and repeatability in measurement of herbal medicines, which was a good alternative to toxic mercury-based electrodes. In particular, the main advantages of the proposed method were low analysis costs, fast response time, very low determination limits, simple operation and low environmental impact.

Experimental

Apparatus

Differential pulse stripping voltammetry was performed with a CHI660A electrochemical workstation (Chenhua Instrumental Corporation, China), in connection with a personal computer. A modified glassy carbon electrode (GCE, 3 mm diameter, BAS) served as a working electrode, with the Ag/AgCl (3 mol \cdot L⁻¹ NaCl) and platinum wire acting as a reference electrode and a 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. Graphite furnace atomic absorption experiment was carried out by a Solaar M6 instrument (Electrothermal Instrument, USA). Cadmium and lead were determined using the following instrumental parameters: drying, 30 s at 100 $^{\circ}$ C; ashing, 20 s at 500 $^{\circ}$ C; atomizing, 10 s at 2500 °C for Cd and 2770 °C for Pb; wavelength at 228.8 nm for Cd and 283.3 nm for Pb, respectively. No deaeration of the solutions was applied at any stages of this study. All potentials were given versus the Ag/AgCl (3 mol \bullet L⁻¹ NaCl) electrode.

Reagents

All the chemicals were of analytical grade. Nafion (w=5% solution in a mixture of water and lower aliphatic alcohols) was purchased from Aldrich. The diluted w=1% Nafion solution was prepared with absolute ethanol. The bismuth(III), lead(II), cadmium(II) and mercury(II) solutions were prepared from 1000 mg•L⁻¹ atomic absorption standard solutions after appropriate

dilution. An acetate buffer solution (0.1 mol \cdot L⁻¹, pH 4.5) served as the supporting electrolyte.

Sample preparation

Herbal medicines (Table 1) were collected randomly from Chinese market. After being divided into small pieces, the samples were dried thoroughly for 12 h in an oven at 60 °C and weighed accurately 1 g for each sample in a 50 mL quartz crucible. The sample was digested by 10 mL of an acid mixture of HNO₃ and HClO₄ (4 : 1, V : V) overnight, and then the solution was evaporated to dryness. The residue was further heated with 5 mL of concentrated HNO₃ until decolorisation. The residue was filtered and diluted to 50 mL with ultrapure water in a plastic volumetric flask.

 Table 1
 Medicinal plants used as samples in this study

 Jinyin Hua Flos Lonicerae Huoxiang Herba Agastachis Fanxie Ye Folium Sennae 	Sample	Chinese name	Latin name	
 Huoxiang Herba Agastachis Fanxie Ye Folium Sennae 	1	Jinyin Hua	Flos Lonicerae	
3 Fanxie Ye Folium Sennae	2	Huoxiang	Herba Agastachis	
	3	Fanxie Ye	Folium Sennae	
4 Caowu Radix Aconiti Kuenezoffii	4	Caowu	Radix Aconiti Kuenezoffii	
5 Danshen Radices Salvia Mitrorrhiza	5	Danshen	Radices Salvia Mitrorrhiza	
6 Dangshen Radix Codonopsis	6	Dangshen	Radix Codonopsis	
7 Fuzi ₁ Radix Aconiti Praeparata	7	Fuzi ₁	Radix Aconiti Praeparata	
8 Fuzi ₂ Radix Aconiti Praeparata	8	Fuzi ₂	Radix Aconiti Praeparata	
9 Huangqi Radix Astragali	9	Huangqi	Radix Astragali	
10 Shanzhu Yu Fructus Corni	10	Shanzhu Yu	Fructus Corni	

Procedure

The glassy carbon electrode was polished with water slurry of 0.05 μ m Al₂O₃, rinsed with water and then dried. A 3 μ L drop of 1% 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 before being used.

2 mL of sample solution was adjusted to pH 4.5 with NaOH and diluted to 5 mL with 0.1 mol \cdot L⁻¹ acetate buffer (pH 4.5). After the treatment, the solution was transferred into an electrochemical cell without deaeration. The three electrodes were immersed into the electrochemical cell with above solution and 800 µg•L⁻ bismuth. Stripping voltammetric measurements were performed with an in situ deposition of the bismuth and Pb and Cd at deposition potential of -1.2 V for 300 s while the solution was stirred. After the solution was left in quiescence for 10 s, differential pulse stripping voltammogram of the solution was recorded by scanning the potential from -1.0 to 0.0 V with amplitude of 50 mV, pulse width of 50 ms and potential step of 4 mV. Prior to the next cycle, a 30 s conditioning step at +0.3 V (with solution stirring) was used to remove the target metals and bismuth. The concentrations of trace metals in all samples under investigation had been calculated by a standard addition method. An in situ plated Nafioncoated mercury film electrode (NCMFE, 800 μ g•L⁻¹ mercury) and a bismuth film electrode (BFE) were used under the similar measurement procedures. All experiments were carried out at room temperature.

Results and discussion

Comparison of the stripping performance of Nafion/GC, BFE and NCBFE

Figure 1 shows the stripping voltammagrams of Pb(II) and Cd(II) at Nafion/GC (a), BFE (b) and NCBFE (c) in the sample solution. As seen in Figure 1, very small and distorted stripping peaks of Pb and Cd were observed on the Nafion/GC (Figure 1a). However, distinct and distorted stripping peaks for analytes were achieved on the BFE when simultaneously electrodepositing bismuth ion along with the target metals on bare GCE (Figure 1b). Moreover, the stripping signals of target metals on NCBFE plated in situ were more remarkable and attractive (Figure 1c). Compared with Nafion/GC and BFE, the electrochemical signals on NCBFE were improved by about 84% and 50% for Pb, and 74% and 20% for Cd, respectively. In addition, the peak potentials of the two metals were shifted to the cathodic direction on both the NCBFE and Nafion/GC. This may be explained that the Nafion coating indeed constituted a separate phase which interacted with the stripping process. The diffusion coefficients in the polymer phase are somewhat lower than those in aqueous solution, but it did not significantly hinder the transport of metal ions to the electrode surface during deposition. The limiting step in the overall mass transport during deposition was the convective-diffusive transport of analyte in the solution. This potential shifts were indicative of coulombic interactions between the cation-exchanging Nafion film and the accumulated metals that affected the redox potential of the latter.¹⁸



Figure 1 Differential pulse stripping voltammograms of 20.8 μ g•L⁻¹ Pb(II) and 7.28 μ g•L⁻¹ Cd(II) at Nafion/GC (a), BFE (b) and NCBFE (c) in a Fructus Corni sample solution. Deposition for 300 s at -1.2 V; "cleaning" for 30 s at +0.3 V; differential pulse voltammetric stripping scan with an amplitude of 50 mV, a pulse width of 50 ms and a potential step of 4 mV.

Comparison of the electrochemical response between NCBFE and NCMFE

Figure 2 shows the typical anodic stripping voltammograms for Pb(II) and Cd(II) at NCMFE (a) and NCBFE (b) in the sample solution. As shown in Figure 2, well-defined and separated peaks of Pb and Cd were observed after 300 s deposition and the sensitivity to Pb and Cd was comparable on the two electrodes. The position of Pb was approximately the same on the two electrodes but Cd peak was shifted to more negative values on the NCBFE. Hence, the resolution between the Cd and Pb peaks was improved on the NCBFE. In addition, it was found that bismuth-coated electrodes were less susceptible to dissolved oxygen interference in contrast to mercury-based electrodes which had to be deaerated by purging water-saturated pure nitrogen and prolonging the analysis time of experiments. The differential pulse scan also resulted in a low 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.



Figure 2 Differential pulse stripping voltammograms of 20.8 μ g•L⁻¹ Pb(II) and 7.28 μ g•L⁻¹ Cd(II) on *in situ* plated NCMFE (a) and NCBFE (b) in the Fructus Corni sample solution. Conditions were the same as those in Figure 1.

It was well known that the utility of mercury as an electrode material in ASV was based on its ability to form amalgams with many metals, while the performance of bismuth could be attributed to its property of forming alloys with different metals.^{19,20} Bi(III) and analytes were reduced and deposited on the electrode surface at a sufficient negative potential during a preconcentration step, and bismuth was able to form alloys with some metals of interest like cadmium and lead, both reactions (1) and (2) took place simultaneously. In the ensuing anodic scan, all metals accumulated onto the electrode surface were reoxidized and stripped off.

$$\mathrm{Bi}^{3+} + 3\mathrm{e}^{-} \to \mathrm{Bi}^{0} \tag{1}$$

$$\mathbf{M}^{n+} + n\mathbf{e}^{-} \to \mathbf{M} (\mathbf{B}\mathbf{i}) \tag{2}$$

Optimization of operation conditions

Effect of deposition potential In the stripping procedure, accurate determination of the elements in natural media was based on the use of deposition potential. In order to get a well defined reduction or oxidation peak, the optimum deposition potential must be obtained. Figure 3 displays the influence of deposition potentials on peak currents of Pb and Cd in the sample solution over the potential range of -0.8 to -1.6 V. As shown in Figure 3, in the range of potential from -0.8 to -1.0 V, the peak current of Pb increased sharply but Cd peak was not observed at -0.8 and -0.9 V, probably due to the incomplete reduction of Cd to form an alloy with the bismuth electrode. The peak current of Pb was approximately the same and the Cd peak gradually increased from -1.0 to -1.2 V, and both Pb and Cd in the sample solution could be deposited efficiently on the NCBFE at -1.2 V. At a more negative potential than -1.2 V, and peak currents of both metals decreased gradually, and it might be assumed that the use of high negative plating potentials resulted in increased surface roughness and hence, in decreased stability of bismuth film. Therefore, -1.2 V was selected as the deposition potential.



Figure 3 Effect of the deposition potential on the peak currents of 20.8 μ g•L⁻¹ Pb and 7.28 μ g•L⁻¹ Cd in the Fructus Corni sample solution. Conditions were the same as those in Figure 1.

Effect of deposition time Figure 4 examines the effect of deposition time on peak heights of Pb(II) and Cd(II) in the range of 0-600 s in the sample solution on *in situ* plated NCBFE. The peak heights increased linearly up to 300 s while at higher deposition time the peak height versus time plots started to deviate from linearity. The observation at long deposition time was caused by the saturation of the NCBFE surface. The stripping peak currents of the two metals increased, but became wider with increasing deposition time longer than 300 s. In this work, deposition time for 300 s was chosen to achieve high sensitivity and save analysis

time.



Figure 4 Effect of the deposition time on the peak currents of 20.8 μ g•L⁻¹ Pb and 7.28 μ g•L⁻¹ Cd in the Fructus Corni sample solution. Conditions were the same as those in Figure 1.

Effect of bismuth ion concentration The bismuth ion concentration had a profound effect on the stripping response to NCBFE. The concentration of Bi(III) ion controlled the thickness of the bismuth film, whereas the thickness of the film did not affect the peak position of any metal. Figure 5 displays the influence of the bismuth concentrations on the electrochemical responses to Pb and Cd in the sample solution. The peak currents of Pb and Cd increased with increasing concentrations of bismuth ion, which were maximum at 800 $\mu g^{\bullet} L^{-1}$ of bismuth ion and started to decrease at higher concentrations of bismuth. The results revealed that the best combination of sensitivity, peak sharpness of Cd and Pb were obtained at Bi(III) concentration of 800 $\mu g^{\bullet} L^{-1}$.

Effect of pH Buffer solution had the ability to fix pH value and ionic strength while adding small amounts of foreign sample solution. In the practical analysis, buffer solution therefore, was widely employed. The effect of pH of deposition/measurement and anodic stripping voltammetric performance of the NCBFE in buffered solutions were examined (Figure 6). As clearly evident, the stripping peak currents increased as pH rose from 3 to 4.5, and then a fast decrease of stripping signals for both target metals was observed at higher pH, which indicated that the use of *in situ* prepared NCBFE at pH above 5 was unfavorable, most probably due to an effect of Bi(III) hydrolysis in a non-complexing acetate medium. Therefore, the optimum performance of the NCBFE was achieved at the pH of 4.5.

Effect of Nafion concentrations The Nafion concentration had a profound effect on the stripping response. All the Nafion-coated electrodes exhibited higher sensitivity than a bare BFE. Another observation



Figure 5 Effect of the bismuth ion concentration on the peak currents of 20.8 μ g•L⁻¹ Pb and 7.28 μ g•L⁻¹ Cd in the Fructus Corni sample solution. Conditions were the same as those in Figure 1.



Figure 6 Effect of pH on the peak currents of 20.8 μ g•L⁻¹Pb and 7.28 μ g•L⁻¹Cd in the Fructus Corni sample solution. Conditions were the same as those in Figure 1.

was related to the fact that the peak current was highest for 1% Nafion modified GCE among all the Nafion solutions at 0.25%, 0.5%, 1%, 1.5% and 2% (not shown). In view of these results, the 1% Nafion solution was selected for further work.

Electrochemical performance of NCBFE

The proposed method of the NCBFE was applied to the determination of trace amounts of Pb(II) and Cd(II) in herbal medicines. The concentration of trace elements in all samples under investigation had been calculated using the standard addition method. The method was chosen because the matrix effects were less influenced by this procedure, which had ability to compensate for proportional systematic errors. Figure 7 illustrates stripping voltammograms for the determination of Pb(II) and Cd(II) in the Fructus Corni sample. It was evident that the well-defined Pb and Cd peaks were observed at -0.55 and -0.78 V, respectively. Successive standard additions of 5 $\mu g {}^{\bullet} L^{-1}$ Pb and Cd caused current increments at the sample potential and made the determination of Pb and Cd in the Fructus Corni sample possible. Figure 8 shows the plots of peak currents versus concentrations of Pb and Cd. A good linearity was obtained in the range of the examined concentrations and can be represented by both the equations of the lines Y =0.0781x + 0.4421 for Pb and Y = 0.041x + 0.0993 for Cd, with correlation coefficients of 0.9978 and 0.9989, respectively. Each point was the mean of the values obtained from five times repeated with the same electrode. In the experimental conditions employed, precisions as repeatability, expressed as relative standard deviations (R.S.D.) on five independent determinations, were satisfactory, being lower than 5% in all cases.



Figure 7 Differential pulse stripping voltammograms of the determination of Pb(II) and Cd(II) in the Fructus Corni sample solution on *in situ* plated NCBFE. From below: sample and successive standard additions of 5 μ g•L⁻¹ Pb(II) and Cd(II). Other conditions were the same as those in Figure 1.



Figure 8 Plots of peak currents of Pb and Cd versus concentrations. Conditions were the same as those in Figure 1.

The reproducibility of the method had an important effect on detecting trace elements in real samples. The reproducibility of the electrode was examined by five independent treatments on the same sample and each solution was analyzed five times. The R.S.D. values of 20.8 μ g•L⁻¹ Pb and 7.28 μ g•L⁻¹ Cd in a real sample, which were determined at one single modified electrode, were 3.2% and 4.8%, respectively. After every measurement, the NCBFE was remade, and the R.S.D. values of 20.8 μ g•L⁻¹ Pb and 7.28 μ g•L⁻¹ Cd were 4.2% and 5.6% (*n*=5). This result suggested that the NCBFE exhibited excellent reproducibility towards the determination of Pb and Cd in herbal medicines.

To demonstrate the validity for the proposed method, further recovery experiments were carried out. A synthetic solution containing Pb(II) and Cd(II) was prepared for the performance of the recovery test. Adding 5 $-10 \ \mu g \cdot L^{-1}$ of Pb and Cd solutions to the sample, and both the spiked and the unspiked samples were analyzed five times by the proposed method. The mean recovery (% ± SD, *n*=5) of the method was summarized in Table 2. The recovery percentages for Pb and Cd in the studied samples were very satisfactory due to the high analytical sensitivity obtained.

 Table 2
 Recoveries of Pb and Cd in the sampled herbal medicines

Sample	Mean recoveries ^{<i>a</i>} $(\% \pm SD)^n$ for Pb/%	Mean recoveries ^{<i>a</i>} $(\% \pm SD)^n$ for Cd/%		
1	101.4 ± 1.20	96.5±0.56		
2	94.2±2.55	97 ± 1.52		
3	96.5 ± 1.45	91.2±2.56		
4	95.6 ± 1.25	92.8 ± 1.15		
5	87.8 ± 1.85	89.5 ± 2.05		
6	88.5 ± 2.25	90.2 ± 1.25		
7	105.4 ± 2.50	102.3 ± 2.05		
8	110.5 ± 1.28	108.5 ± 2.12		
9	99.2 ± 0.75	$95.6 {\pm} 0.95$		
10	100 ± 1.15	98.5 ± 0.96		

^{*a*} Mean of five replicate measurements at a 95% confidence level. ^{*n*} Number of experiments, n=5.

In the case of voltammetric technique, since the analytical calibration functions were determined by the standard addition method, it was possible to obtain the limits of determination (LOD) directly in the real matrices. The limits of determination were calculated to be $0.35 \ \mu g^{\bullet} L^{-1}$ for Pb and $0.72 \ \mu g^{\bullet} L^{-1}$ for Cd (*S*/*N*=3).

It is well known that the surfaces of solid electrodes, such as glassy carbon, tend to become blocked over time when applied to detect analytes in natural media due to irreversible adsorption of electroactive and other chemical species, leading to a decrease in response and difficulties in the analysis of untreated samples.¹⁸ Modifying or protecting the electrode surface can lead to minimization of such factors for electroanalysis. The commonest polymer is Nafion, which is nonelectroactive, hydrophilic and insoluble in water. It possesses several ideal properties as permselective material and represents sufficiently good discrimination against potential adsorbents and interfering species.²¹ Moreover, the formation of a Nafion coating on the electrode surface is straightforward, easy and fast. The tolerance for surface-active compounds, such as Triton X-100 (10 $mg \bullet L^{-1}$) and tetrabutylammonium bromide (10 mg \bullet L^{-1}), was studied. It has been demonstrated that the permselective Nafion film on the NCBFE can significantly improve tolerance to surfactants and stability of the NCBFE. In addition, the Nafion film acting as a cation-exchanger facilitates the non-faradaic preconcentration of metal cations, and also helps to confine the stripped metals close to the electrode surface where more efficient replating can occur during the reverse pulse.¹⁸ Therefore, the presence of the Nafion film may account for the improvement in sensitivity on the NCBFE.

Data for herbal medicines by DPASV and comparison with GFAAS measurements

The NCBFE was applied to Pb and Cd determinations by DPASV in ten different commercial samples of herbal medicines. To better validate the voltammetric analytical procedure proposed, the metal concentrations have been also determined by GFAAS. The experimental confirmation of such a validation was the results reported in Table 3, suggesting that there was a satisfactory agreement between the two techniques, with relative errors lower than 6.5% in all samples. Of all the herb samples, the highest Pb content was found in the sample 7 with 4.21 mg•kg⁻¹, while in sample 1 the Pb content was as low as 1.80 mg•kg⁻¹. Sample 7 also had the highest Cd content value $(0.412 \text{ mg} \cdot \text{kg}^{-1})$ and sample 1 showed the lowest Cd value $(0.12 \text{ mg} \cdot \text{kg}^{-1})$. The maximum permissible concentrations of heavy metals in herbal medicines were 5 mg•kg⁻¹ for Pb and 0.3 mg• kg^{-1} for Cd dry weight set by Chinese Ministry of Health.²² Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) fixed weekly intake limits of 25 μ g•kg⁻¹ of body weight for adults for Pb and 7 μ g•kg⁻¹ for Cd.^{23,24} The analytical results obtained for Pb indicated that it was present at a concentration below the permitted level, but levels of Cd found in the five studied samples (sample 5, 0.324 $mg \cdot kg^{-1}$; sample 6, 0.356 $mg \cdot kg^{-1}$; sample 7, 0.412 $mg \cdot kg^{-1}$; sample 8, 0.364 $mg \cdot kg^{-1}$; and sample 9, 0.378 $mg \cdot kg^{-1}$) exceeded the allowable limits. The high content of Cd found in the products in this study may be caused by intrinsic toxicity, contaminated soils, consumption of fuel, incorrect preparation, and failure of good manufacturing practice. The results suggest that authorities may need to institute regulations to minimize toxic element contents and good manufacturing practice rules may need to specifically address the issue of toxic element contamination in herbal medicines.

Conclusion

Based on the results obtained in the present work, it

Table 3	Results for the determination of Pb and Cd in ten herbal medicines b	y DPASV a	nd GFAAS (mg•kg ⁻¹)
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Sample -	Ι	Pb (<i>n</i> =5)			$\operatorname{Cd}(n=5)$	
	DPASV ^a	GFAAS ^a	$e_{\rm r}^{\ b}$	DPASV ^{<i>a</i>}	GFAAS ^a	$e_{\rm r}^{\ b}$
1	1.80 ± 0.05	1.73 ± 0.06	4.1	0.120 ± 0.03	0.117 ± 0.04	2.6
2	2.76 ± 0.09	2.95 ± 0.05	-6.4	0.180 ± 0.02	0.175 ± 0.02	2.9
3	1.86 ± 0.07	1.81 ± 0.08	2.8	0.125 ± 0.025	0.121 ± 0.018	3.3
4	3.22 ± 0.15	3.15 ± 0.14	2.2	0.216 ± 0.018	0.224 ± 0.021	-3.6
5	2.93 ± 0.10	3.01 ± 0.08	-2.7	0.324 ± 0.025	0.312 ± 0.028	3.8
6	2.19 ± 0.08	2.11 ± 0.07	3.8	0.356 ± 0.032	0.372 ± 0.038	-4.3
7	4.21 ± 0.18	4.08 ± 0.16	3.2	0.412 ± 0.035	0.428 ± 0.028	-3.8
8	2.30 ± 0.06	2.23 ± 0.04	3.1	0.364 ± 0.017	$0.351 \!\pm\! 0.016$	3.7
9	2.93 ± 0.06	3.02 ± 0.05	-3.0	0.378 ± 0.021	$0.395 \!\pm\! 0.025$	-4.3
10	1.98 ± 0.07	2.02 ± 0.08	-2.0	0.285 ± 0.018	0.278 ± 0.016	2.5

^a Mean of five replicate measurements at a 95% confidence level, mean ± SD%; ^b Relative error; n: Number of experiments.

can be concluded that the proposed method was suitable for the determination of heavy metal concentrations in phytopharmaceuticals. The simplicity and versatility of the procedure made it attractive for its use in the pharmaceutical quality control of medicinal plants. In particular, the selectivity of this electrode for simultaneous analysis of heavy metals opened the possibility to consider the bismuth film electrodes as good alternative to toxic mercury-based electrodes. Combined with the unique property and simple formation of the Nafion coating, it can extend the scope and utility of bismuth film electrodes.

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