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BISMUTH FILM ELECTRODE FOR MEASUREMENT OF TRACE LEAD BY ADSORPTIVE STRIPPING VOLTAMMETRY WITH CALCEIN BLUE

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ABSTRACT

In situ plated bismuth film electrode was developed for adsorptive stripping voltammetric determination of trace lead, using Calcein Blue as complexing ligand. The sensitivity of the method was improved by two-period accumulation (deposition and adsorption) of Pb^{II} - Calcein Blue complex on the electrode. Under suitable conditions (1 μ M Calcein Blue, 100 mM TRIS, pH 7.5, deposition at - 1100 mV for 120 s, adsorption at - 200 mV), the 3 σ detection limit of 0.36 ppb Pb^{II} after the adsorption time of 10 s was obtained. Copper, cadmium and zinc had no significant interference. The method was successfully applied to river water.

Keywords: Stripping voltammetry; Bismuth film; Lead

INTRODUCTION

Stripping voltammetry attain a great sensitivity in detection of trace metals in environmental and biological samples. Many stripping voltammetric methods were reported for reliable determination of trace lead (Fischer E. and van den Berg, 1999; Locatelli and Torsi, 2000; Barberia and Stradiotto, 1997). In particular, adsorptive stripping voltammetry (AdSV) with selective complexing reagents was considered to be one of the most sensitive methods. Most of the AdSV determination of lead to date has been based on the use of hanging mercury drop electrode (HMDE) (Wang et al., 1993; Wu and Batley, 1995) or mercury film electrode (MFE) (Limson and Nyokong, 1997). Many complexing ligands were found to sensitively detect lead, such as o-cresolphthalexon (Wang et al., 1993), xylenol orange (Wu and Batley, 1995), substituted catechols (Limson and Nyokong, 1997)... Yokoi et al. (1995) found that Calcein Blue (8-[N,N-bis(carboxymethyl)aminomethyl]-4-methylumbelliferone) is suitable as complexing ligand for AdSV determination of lead in fresh water on HMDE with high selectivity (3 σ detection limit of 0,04 nM after 1 min collection). However, owing to much environmental concern, development of mercury-free electrodes for stripping voltammetry may attract interest. Recently, a new working electrode, bismuth film plated in situ on the surface of glassy carbon disk electrode (in situ BiFE), have developed for anodic stripping voltammetric determination of copper, lead, cadmium and zinc (Wang et al., 2000, 2001). However, the strong interference of copper to the stripping response of lead, cadmium and zinc on in situ BiFE lowered sensitivity of their measurement and this problem has not been overcome. For removal of the copper interference, chloroform extraction of Cu^{II} - dithizone complex from analytical solution before ASV determination of lead on in situ BiFE was suggested by Khanh and Hop (2002). Bismuth is a metal with a very low toxicity and less environmentally concern. Besides, understanding of bismuth electrode to date has been limited, so that further studies on its characteristic and application are of necessity and interest.

In this paper we report studies on the use of in situ BiFE for AdSV determination of Pb^{II} with Calcein Blue (CB). By this way, the interference of copper mentioned above in anodic

stripping voltammetry will be overcome and then selectivity of the stripping voltammetric measurement of lead on bismuth film electrode will be improved.

EXPERIMENTS

Instrumentation

A polarographic analyzer consists of a 694 VA Stand and a 693 VA Processor (Metrohm, Switzerland). The 694 VA Stand consists of three-electrode configuration with a glassy carbon (GC) working electrode (2.8 ± 0.1 mm diameter), an Ag/AgCl (KCl sat.) reference electrode and a platinum wire auxiliary electrode. The 693 VA Processor is operated by the software available with this instrument, which enable the development of complete analytical procedures including control of deposition potential, deposition time and rotating rate of working electrode, recording voltammograms...

Reagents

Working solutions of Bi^{III} , Cu^{II} , Pb^{II} , Cd^{II} , Zn^{II} were prepared from 1000 ppm Merck atomic absorption standard solutions and double-distilled water (water distiller Fistream Cyclon, England). An 1M TRIS (2-amino-2-hydroxymethyl-1,3-propanediol) buffer solution in 0.4M HCl (pH 7.5) served as the supporting electrolyte. CB solution was prepared from Dojindo (Japan) in 0.01M KOH. Other chemicals were of analytical reagent grade (Merck).

PROCEDURE

Working electrode

The glassy carbon disk electrode was cleaned and polished to a mirror-like finish with 0.05 μm alumina slurry, and then rinsed with acetone and water. The *in situ* bismuth film was formed together with accumulation of under study metal on the surface of the electrode during deposition step. After each measurement cleaning the electrode was made by applying the potential of 300 mV to strip bismuth and other metals from the surface of the electrode. After a series of measurement the electrode was cleaned by wiping the rotating electrode with a wet tissue and then, rinsing with water.

Determination of Pb^{II}

The glassy carbon disk electrode was put into the cell containing analytical solution, 0.1M TRIS buffer solution (pH 7.5), 1 μM CB complexing ligand solution and 200 ppb Bi^{III} . The final volume of the solution in the cell was 10 mL. The solution was not deaerated. Deposition of bismuth and the metal/metals under study onto the surface of the GC electrode was carried out at -1100 mV (E_{dep}) for 120 s (t_{dep}), while the solution was stirred by rotating the electrode at the speed of 1600 rpm (ω). After that, the rotation of the electrode was turned off and left for $10 \div 20$ s (t_{rest}), that the solution became quiescent, then an adsorption potential ($E_{\text{ad}} = -200$ mV) was applied to the electrode for 20 s (t_{ad}). Stripping step was made in differential pulse mode starting from the adsorption potential (-200 mV) to -1100 mV with a scan rate of 20 mV/s (v) in negative direction. Parameters of differential pulse voltammetry included a pulse width of 40 ms (t_{pulse}), a pulse height of 50 mV (U_{pulse}), measuring time of 20 ms (t_{meas}), and an increment of 6 mV (U_{step}). The amount of the metal was made by standard addition method ($4 \div 5$ additions). Duplicate runs were performed on blank, each analytical solution and the solution after each standard addition, and then an average was calculated from the two runs. The analytical current-potential response recorded is peak form.

RESULTS AND DISCUSSION

Voltammetric characteristics of lead on *in situ* BiFE in the presence of CB

Fig. 1 shows cyclic voltammogram for 500 ppb Pb^{II} on *in situ* BiFE (in a TRIS buffer solution containing 250 ppb Bi^{III} and complexing ligand CB). One cathodic peak is observed at -450 mV during the negative-going scan. Scanning in the reverse direction exhibits a smaller and broader anodic peak (at -500 mV). The response for Pb^{II} increases dramatically when a two-period accumulation (deposition and adsorption) preceded the potential scan, indicating an effective interfacial accumulation of the Pb^{II} - CB complex. No response was observed for analogous measurements without the ligand (not shown). The Pb^{II} - CB complex appears to be more strongly absorbed at the BiFE than Pb^{II} - Oxine at the same experimental conditions (not shown).

The two-period accumulation gained sensitivity higher than the case of conventional adsorption (at a adsorptive potential of -300 mV for 20 s, without pre-deposition of lead at a deposition potential of -1100 mV for 120 s; the cyclic voltammogram not shown). Therefore, two-period accumulation of Pb^{II} - CB complex can be used as an effective pre-concentration step prior to the voltammetric measurements on BiFE. By this way, highly sensitive adsorptive stripping measurements of lead on BiFE can be achieved. Besides, simple preparation of *in situ* BiFE supports its development and application for stripping voltammetry.

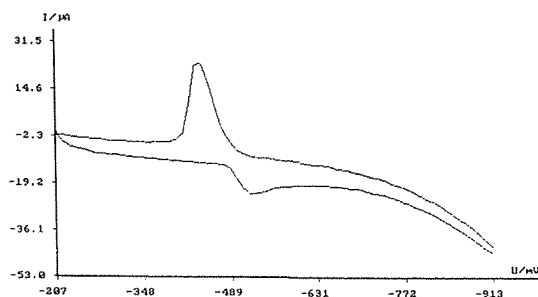


Fig. 1. The cyclic voltammogram for a solution containing 500ppb of Pb^{II} on *in situ* BiFE.

Conditions: 250ppb Bi^{III} ; 10 μ M calcein blue; supporting electrolyte, TRIS 0,1 M (pH = 7.5); deposition time (t_{dep}), 120s; deposition potential (E_{dep}), -1100mV; rotating rate (ω), 1600rpm; adsorption potential (E_{ad}), -200mV; adsorption time (t_{ad}), 20s; range of potential scan (E_{range}), -200mV \div -1000mV; scan rate (v), 100 mV/s.

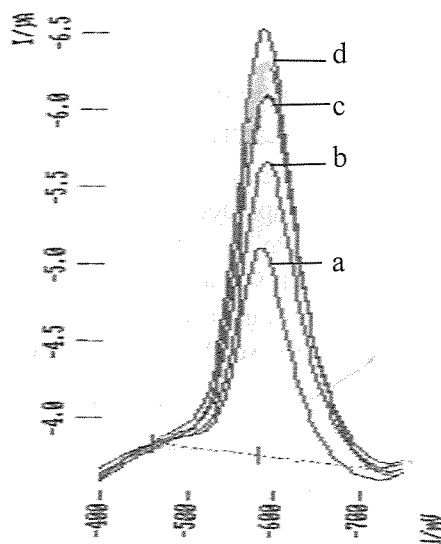


Fig. 2. Stripping voltammograms for 5 ppb Pb^{II} on *in situ* BiFE: a,b,c,d. standard additions, each 2 ppb of Pb^{II} .

Conditions: 200ppb Bi^{III} ; 10 μ M calcein blue; 100mM TRIS (pH = 7.5); E_{dep} = -1100mV; t_{dep} = 100s; E_{ad} = -200mV; t_{ad} = 10s; rest time (t_{rest}), 10s; E_{range} = -200mV \div -1100mV; v = 20mV/s; pulse amplitude (ΔE), 50mV; pulse time (t_{pulse}), 40ms; measurement time (t_{meas}), 20ms; voltage step (U_{step}), 6mV; rotating rate (ω), 1600rpm.

Effect of pH and supporting electrolyte concentration

The effect of pH on the peak current of lead was examined in solution containing 250 ppb Bi^{III} , 10 ppb Pb^{II} , 10 μM CB and 0.1 M TRIS. The peak current of lead decreased rapidly at pH less than 6.0 and higher than 7.5. The optimum response obtained at a pH between 6.0 and 7.5.

The stripping response of lead increased with the increase in TRIS concentration from 5 to 100 mM (pH = 7.0), then decreased at the concentration above 100 mM. The peak potential shifted anodically about 10 mV. A concentration of 100 mM TRIS was selected as suitable for future experiments.

Effect of Bi^{III} concentration for in situ plating

The adsorption of Pb^{II} - CB complex (at the concentration of 5 ppb Pb^{II}) on *in situ* BiFE was not efficient at the concentration of Bi^{III} less than 100 ppb and so that the lead peak current decreased. At the concentration of Bi^{III} higher than 300 ppb, the lead peak got broader or double, decreasing resolution (for neighboring peaks). This broad (or double) peak might be the result of the reduction of Bi^{III} -CB complex, which was adsorbed onto the surface of the electrode (in step of adsorption at potential -200mV), or of the reduction controlled by diffusion. The lead peak potential shifted anodically about 10 mV with the increase in Bi^{III} concentration from 100 to 500 ppb. A concentration of 200 ppb Bi^{III} was suitable for adsorptive stripping voltammetry of Pb^{II} on *in situ* BiFE.

At the concentration of 200 ppb Bi^{III} , the linearity between the peak current and Pb^{II} concentration was good ($R = 0.999$; see Fig. 2).

Effect of complexing ligand concentration

Adsorption of Pb^{II} - CB complex (at 2 ppb Pb^{II} concentration) was found to increase with increasing CB concentration, reaching a maximum above 0.9 μM . The increase in peak current was accompanied by a positive shift (about 10 mV) in the peak potential for the reduction of the Pb^{II} - CB complex. At CB concentration higher than 1 μM , competitive adsorption between CB and Pb^{II} - CB complex on the surface of the working electrode might be occurred, resulting in decrease in the lead peak current. CB concentration of 0.9 -1.0 μM was appropriate for AdSV measurement of lead.

Effect of the deposition potential and deposition time

The peak current of lead increased with the cathodic increase in deposition potentials from -900 mV to -1300 mV. The peak potential shifted anodically about 20 mV. At the deposition potentials more negative than -1100 mV, the simultaneous accumulation of lead and other metals (Zn^{II} , Ni^{II} , Co^{II} ...probably present in analytical sample) can occur, modifying the surface of the electrode (e.g. forming binary alloy and/or intermetallic compound) and decreasing reproducibility of the measurement. The accumulation of lead decreased for the deposition potentials more positive than -1100 mV. The potential of -1100 mV is appropriate for the deposition of lead on *in situ* BiFE.

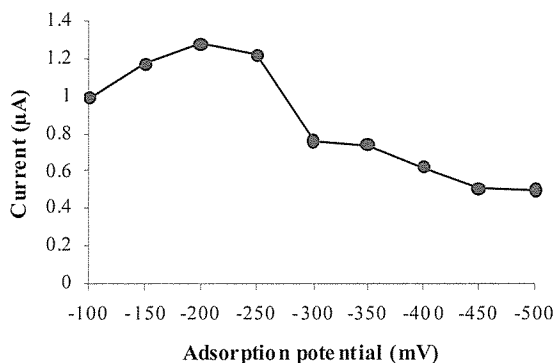


Fig. 3. Effect of the adsorption potential (E_{ad}) on the stripping peak of lead

Conditions: 5ppb Pb^{II} ; 200 ppb Bi^{III} ; 1 μM CB; 100 mM TRIS (pH = 7.5); $t_{\text{dep}} = 120\text{s}$; $E_{\text{dep}} = -1100\text{mV}$; adsorption time (t_{ad}), 10s; other conditions as Fig.2.

The lead peak increased with the increase in deposition time. In this study, a deposition time of 120 s was suitable for the concentration of 5 ppb Pb^{II}. Increasing the deposition time lengthens analytical time and may accumulate other metals, modifying the surface of the electrode.

Effect of adsorption potential and adsorption time

After the deposition of lead on *in situ* BiFE, the rotation of the electrode was turned off and left for 10 ÷ 20 s, that the solution became quiescent. Then an adsorption potential was applied to the electrode for defined time (adsorption time). During adsorption time, lead (Pb) was oxidized into Pb^{II}, complexing with CB and adsorbing immediately on the surface of the electrode. By the two-period accumulation, efficiency of the adsorption step was improved.

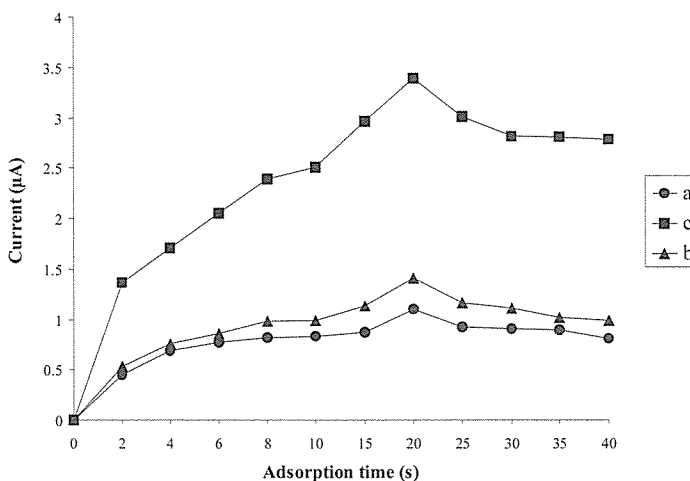


Fig. 4. Effect of the adsorption time (t_{ad}) on the stripping peak of lead: a. 5 ppb; b. 5ppb; c. 10ppb Pb^{II}

Conditions: $E_{ad} = -200\text{mV}$; other conditions as Fig.3.

The effect of adsorption potential on the stripping peak of lead was shown on Fig. 3. Efficiency of the adsorption decreased for the potentials more negative than -200 mV (because of decrease in the lead oxidation). At the potential more positive than -200 mV, the dissolution of bismuth film occurred, resulting in decrease in the adsorption. The potential of -200 mV was selected as optimum.

The effect of the adsorption time on the lead peak was examined in the solutions containing 5 ppb and 10 ppb Pb^{II}. The lead peak reached a plateau at 20 s (see Fig. 4), indicating the adsorption saturation. The time of 20 s was suitable for the adsorption of the Pb^{II} - CB complex on *in situ* BiFE.

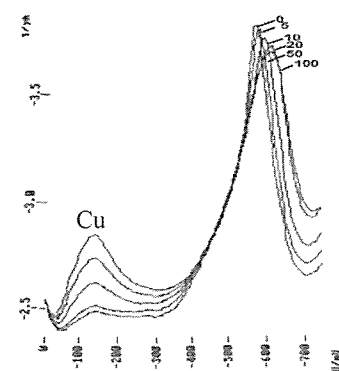


Fig. 5. Influence of copper on the stripping response of lead: 0,5,10,20,50,100. Cu^{II}/Pb^{II} ratio (ppb/ppb).

Conditions: $E_{ad} = -200\text{mV}$; $t_{ad} = 20\text{s}$; 2ppb Pb^{II}; other conditions as Fig.3.

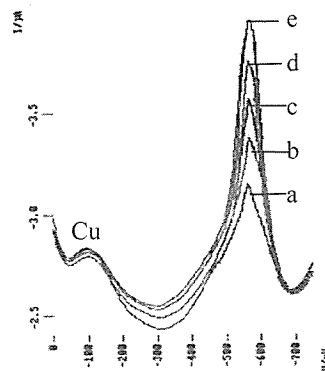


Fig. 6. Stripping voltammograms for the initial Cu^{II}/Pb^{II} ratio (ppb/ppb) of 100: a,b,c,d,e. standard additions, each 2 ppb Pb^{II}.

Conditions: $E_{ad} = -200\text{mV}$; $t_{ad} = 20\text{s}$; 200ppb Cu^{II}; other conditions as Fig.3.

Interferences

The strong influence of copper on the stripping response of lead in anodic stripping voltammetry on BiFE lowered sensitivity of lead measurement (Wang et al., 2000, 2001). Interestingly, in

adsorptive stripping voltammetry with complexing agent CB, the influence of copper on the lead peak was not significant. The resolution between copper peak (at the potential of -150 mV) and lead peak was good (see Fig. 5). At the $\text{Cu}^{\text{II}}/\text{Pb}^{\text{II}}$ ratio (ppb/ppb) of 50 and 100, the lead peak was lowered by 13% and 27% respectively. The linearity between the lead peak and Pb^{II} concentration at the $\text{Cu}^{\text{II}}/\text{Pb}^{\text{II}}$ ratio (ppb/ppb) of 100 was good ($R = 0.998$) (see Fig.6).

Also, cadmium has no significant influence on the stripping response of lead. At $\text{Cd}^{\text{II}}/\text{Pb}^{\text{II}}$ ratio (ppb/ppb) of 100, the lead peak was lowered by 2.1% only and the resolution between lead peak and cadmium peak (at the potential of -900mV) was good. We found that at the above experimental conditions, cadmium can be sensitively measured by AdSV with CB on *in situ* BiFE.

The effect of zinc on the lead stripping response was tested for $\text{Zn}^{\text{II}}/\text{Pb}^{\text{II}}$ ratio (ppb/ppb) of 200. In the potential scanning range from -200mV to -1100 mV, the zinc peak was not appeared. Therefore, the interference of zinc on the lead peak was negligible.

The interference of Triton X-100, a typical non-ionic surfactant, on the stripping response of lead was examined at 2 ppb Pb^{II} concentration. At the concentration of 5 ppb Triton X-100, the lead peak disappeared, because of considerable absorption of Triton X-100 on bismuth film. This will affect labile lead measurements and can be eliminated in total measurements by the UV irradiation step.

Reproducibility, sensitivity, detection limit and linear range

The reproducibility of the stripping response of lead was assessed by carrying out a series of the measurements on the same glassy carbon electrode (see Fig.7). For a solution containing 10 ppb Pb^{II} , the reproducibility in terms of the relative standard deviation (RSD) was 0.1% ($n = 9$).

The sensitivity and detection limit (3σ) was 170 ± 10 nA/ppb and 0.36 ppb, respectively (200 ppb Bi^{III} ; $E_{\text{dep}} = -1100$ mV; $t_{\text{dep}} = 120$ s; $E_{\text{ad}} = -200$ mV; $t_{\text{ad}} = 10$ s). With this detection limit, the AdSV procedure can be used for determination of trace lead in environmental samples.

The linearity was good in the range of 2 ÷ 100 ppb Pb^{II} ($R = 0.973$).

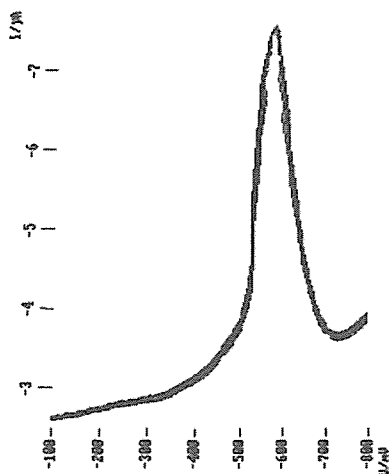


Fig. 7. A series of 9 stripping voltammograms for 10 ppb Pb^{II} was recorded on *in situ* BiFE.

Conditions: 200 ppb Bi^{III} ; $E_{\text{ad}} = -200$ mV; $t_{\text{ad}} = 20$ s; other conditions as Fig.3.

Finally, it can be seen that there is a rather good agreement (see Table 1) between the suitable conditions found in AdSV procedure with CB on HMDE (obtained by Yokoi et al., 1995) and on *in situ* BiFE (obtained in this study). According to us, in many studies on AdSV for trace metals, the suitable conditions on HMDE may be also used for *in situ* BiFE. Note that in Yokoi's study, TES (N-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid and sodium citrate were used as supporting electrolytes and deaeration was carried out prior to deposition step. An advantage of *in situ* BiFE over HMDE was that it may not need to deaerate the analytical solution for AdSV determination of lead and so that it allow to reduce analytical time.

APPLICATION

The AdSV described above was applied to river water (Huong river in Hue city, Vietnam). The river water sample (taken on 18th June, 2004) was acidified with concentrated HNO_3 (2

mL /1 L sample, pH 2) and stored in cleaned PET bottle. For comparison, ASV determination of lead on *in situ* MFE (mercury film electrode) with deaeration was made for the sample. The data given in Table 1 shown that there was a good agreement between the results obtained by AdSV on *in situ* BiFE and ASV on *in situ* MFE. Stripping voltammograms for the two cases were shown on Fig. 8.

Table 1. Pb^{II} found in Huong river water

Sample	Found / ppb (*)	
	<i>in situ</i> BiFE	<i>in situ</i> MFE
Huong river water sample	1.0 ± 0.2	1.1 ± 0.3
Huong river water sample spiked with 2 ppb Pb ^{II}	3.2 ± 0.4	3.4 ± 0.5

(*) mean ± standard deviation (n = 3)

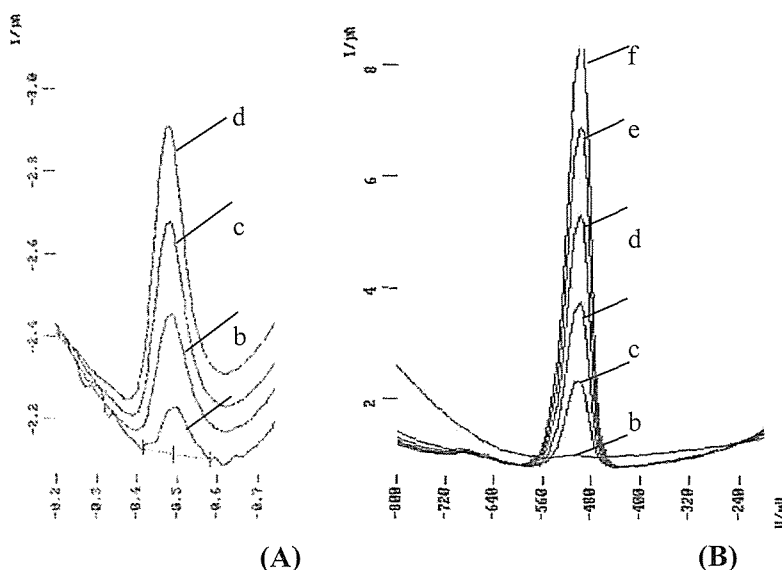


Fig. 8. Determination of Pb^{II} in a river water sample on:

- (A). *In situ* BiFE (non-deaeration); Conditions: 200 ppb Bi^{III}, 10 μ M calcein blue, 100mM TRIS (pH = 7.5), $E_{dep} = -1100$ mV, $t_{dep} = 120$ s, $E_{ad} = -200$ mV; $t_{ad} = 20$ s ; other conditions as Fig.3.
a. sample; b,c,d. standard additions, each 2 ppb Pb^{II}
- (B). *In situ* MFE (deaeration); Conditions: 0.1 mM Hg^{II}, 0.1 M acetate buffer (pH = 4.5), $E_{dep} = -1200$ mV, $t_{dep} = 120$ s; other conditions as Fig.2.

CONCLUSION

In situ BiFE can be used for sensitive measurement of trace lead by AdSV with Calcein Blue as a complexing ligand. At the suitable conditions, this procedure can also be applied to detect trace lead and cadmium in environmental samples. The data obtained above confirm that the stripping voltammetry performance of bismuth electrodes compares favorably to that of mercury electrodes. In particular, bismuth electrodes should facilitate on-site environmental testing of heavy metals, and the development of disposable metal sensors. However, more efforts should be made to further explore the scope and power of bismuth electrodes for stripping voltammetry.

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