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BISMUTH FILM ELECTRODE FOR STRIPPING VOLTAMMETRIC DETERMINATION OF BLOOD LEAD AND PRELIMINARY ASSESSMENT OF BLOOD LEAD LEVEL IN THE RESIDENTS AT CANH DUONG VILLAGE, THUA THIEN HUE PROVINCE

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Abstract

Bismuth film electrode (BiFE) of less environmentally concern was developed to determine blood lead by anodic stripping voltammetry (ASV). The lead determination gained high reproducibility (RSD < 4.5%, n = 2) and low detection limit (0.7 ppb), that were not worse than those on mercury film electrode (MFE). The acurracy of the lead dertermination (recovery 98 – 100.6%) was good agreement with GF-AAS determination ($p > 0.05$). The ASV using BiFE prepared *in situ* were applied for determination of blood lead and 24-hour urine lead of suspected and control group of the residents at Canh Duong village, Thua Thien Hue province. The blood lead level in the suspected group (fishermen, fishing-net repairers and weavers holding small lead pieces in their mouth during fishing-net weaving) were 34.7 ± 28.2 µg/dL (mean ± SD, n = 30), higher than that of the control group (mean ± SD = 16.3 ± 5.1 µg/dL, n = 10). For both groups, 37 out of 40 blood samples (92.5%) had lead level higher than WHO's recommended level (10 µg/dL). This was an evidence on high lead exposure in the suspected group in the study area. Difference between the lead level in 24-hour urine of the suspected group and control group was statistically insignificant ($p > 0.05$). Correlation between the blood lead and 24-hour-urine lead in the residents under study was not found (R = 0.24).

***Keywords*:** Bismuth electrode; Blood lead; Stripping voltammetry.

1. Introduction

Stripping voltammetry was reported for reliable and sensitive determination of trace metals in environmental and biological samples (Fischer E. and van den Berg,1999; Locatelli and Torsi, 2000; Barberia and Stradiotto, 1997). Most of stripping voltammetric determination of lead to date has used hanging mercury drop electrode (HMDE) or mercury film electrode (MFE). However, owing to high toxicity and environmental concerns of the mercury electrodes, 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 (ASV) determination of copper, lead, cadmium and zinc (Wang et al., 2000, 2001; Kefala et al., 2003; Demetriades, 2004). Also, *in situ* BiFE has successfully applied to adsorptive stripping voltammetric (AdSV) determination of Co^{II} (Hutton et al., 2004), Ni^{II} (Wang and Lu, 2000); Pb^{II} (Hop et al., 2004); Cr^{VI} (Lin et al., 2005) and Mo^{III} (Wang et al, 2006). Owing to specific advantages such as environmentally friendly, suitable for FIA or field measurement, and disposable at field (Economou, 2005; Wang, 2005), BiFE has drawn attention of many analysts from the year 2000 forward.

In our previous study, ASV with *in situ* BiFE was used for determination of lead in natural water and Oriental medicament samples (Hop et al., 2003). In this study, *in situ* BiFE was applied to ASV

determination of lead in blood and 24-hour urine samples collected from the residents at Canh Duong village, Thua Thien Hue province, Vietnam. In addition, preliminary assessment of blood lead level in the residents was made, because blood lead has been considered as a good indicator for lead exposure (Goldfrank's, 2002).

Canh Duong village, a one of the poor areas located at coastal region (Figure 1), has 6,300 inhabitants (data of the year 2005), of which 20% population have lived on fishery (the rate of the year 2005 in the whole province was 20% of total population, equal to about 57,000 inhabitants). Fishermen, fishing-net repairers and weavers at the village particularly and the province generally have exposured to lead, due to their habit of holding small lead pieces in their mouth during fishing-net weaving. According to our survey, at average, the fishing-net weavers held about 30 – 60 kg of small lead species during 100 – 200 hours annually. Although several clinical symptoms relative to lead exposure have appeared at many people at the village for years, no study of lead exposure level has been carried out to date.

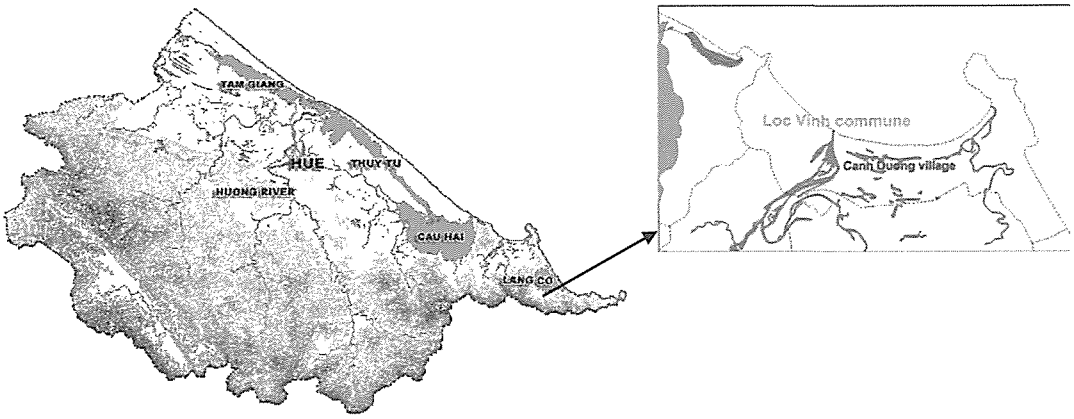


Figure 1. Study area - Canh Duong village, Loc vinh commune, Phu loc district, Thua Thien Hue province

2. Experimental

2.1. Instrumentation and chemicals

A polarography analyzer system 797 VA Computrace (Metrohm, Swiss) with three-electrode configuration (disk glassy carbon working electrode with a diameter of 2 ± 0.1 mm, Ag/AgCl/KCl sat. reference electrode and Pt wire auxiliary electrode) 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... The instrument was also fitted with a Teflon purge tube for deaeration of solution with purified nitrogen (99.999 % nitrogen generator, Whatman, USA).

For comparison, Graphite Furnace - Atomic Absorption Spectrometry (GF-AAS) AAL 6800 (Shimadzu, Japan) used also for determination of lead by calibration curve method with lamp mode BGC-D2 and the following parameters: wavelength 283.3 nm, slid width 0.5 nm and sample atomization at 1800°C in 3 s.

Ultra pure water (Mili-Q test) was used for reagent solution preparation and glassware cleaning and rinsing. All chemicals used were of analytical grade (Merck, Germany).

2.2. Sampling and sample treatment

Blood and 24-hour urine samples were collected in two sessions at Canh Duong village:

- In the first one (10 August 2004), 25 blood samples taken from two groups:
  - Suspected group (fishermen/fishing-net weavers) consisting of 19 persons: 15 men of age 21 – 47 (average 34) and seniority 3 - 31 (average 12); 4 women of age 42 – 62 (average 55) and seniority 6 - 45 (average 24);
  - Control group (non-fishermen/non-fishing-net weavers) including 6 persons: 2 men of age 36 – 39 and 4 women of age 32 - 49;
- In the second one (24 October 2005), blood samples and 24-hour urine samples taken from 15 selected persons out of the above 25 persons of the two groups (in the first session): 11 persons from suspected group (7 men and 4 women) and 4 persons from control group (2 men and 2 women);

Several drops of Heparin was added into the blood samples collected. Then all the blood and 24-hour urine samples were stored in clean PP bottles at deep freezer (– 20°C).

Prior to analysis, the blood (1.0 mL) or 24-hour urine sample (1.0 mL) was digested in conc. HNO_3 (2.0 mL) in closed PTFE (Teflon) bomb placed in oven at 100°C for one hour. Blanks were prepared from ultra pure water by the same way.

2.3. Stripping voltammetric procedure

Working electrode preparation (*In situ* BiFE):

Bismuth film was plated *in situ* onto the surface of disk glassy carbon electrode (GC electrode) in analytical solution containing 100 ppb Bi^{III} and substrate (0.1 M acetate buffer, pH 4.5) at a deposition potential of -1200 mV for deposition time of 90 s. In this step, the GC electrode was rotated at a constant speed (1600 rpm) and lead metal was deposited on the *in situ* BiFE. After each measurement, the bismuth film on the surface of the GC electrode was electrochemically stripped off by applying a potential of + 300 mV to the electrode for 30 s. After a series of measurement the electrode was cleaned by wiping the rotating electrode with a wet tissue and then, rinsing with water.

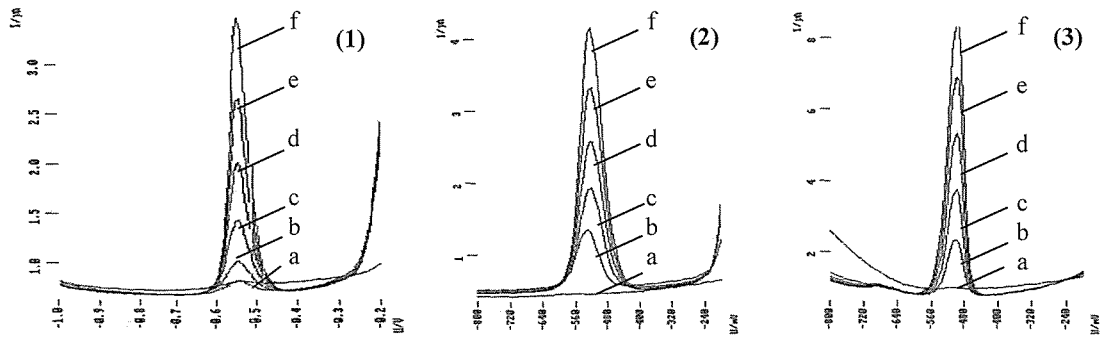
ASV procedure for lead determination on in situ BiFE:

For the procedure, we accepted suitable experimental conditions obtained from previous study (Hop et al., 2003). Analytical solution containing Pb^{II}, Bi^{III} and acetate buffer solution was put into a cell with three electrodes. Final volume of the analytical solution in the cell was 10 mL. A deposition potential (E_{dep}) of -1200 mV was applied to the GC electrode for 90 s (t_{dep}), while the solution was stirred by rotating the electrode at a speed (ω) of 1600 rpm. After that, the electrode rotation was turned off and left for 15 s, that the solution became quiescent, then stripping step was made in differential pulse (DP) mode starting from -1200 mV to +300 mV with a scan rate of 20 mV/s (v) in positive direction. Parameters of DP mode were as follows: pulse width (t_{pulse}) of 40 ms, pulse height (U_{pulse}) of 50 mV, an increment (U_{step}) of 6 mV and measuring time (t_{meas}) of 20 ms. The analytical current-potential response (stripping voltammogram) recorded is peak form. Quantitation of lead was made by standard addition method (3 ÷ 4 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. After each run, the surface of GC was electrochemically cleaned at a potential of + 300 mV for 30 s to strip off bismuth, lead and other metals (if any). The same procedure was done for blanks.

3. Results and discussion

3.1. Influence of interference

Influence of dissolved oxygen



Figer 2. Stripping voltammograms of lead on (1) *In situ* BiFE (dearation);
(2) *In situ* BiFE (non-deaeration);
(3) *In situ* MFE (deaeration; 100 ppm Hg^{II}):
a. blank; b, c, d, e, f. standard additions, each 2 ppb Pb^{II}.
Conditions: 100 ppb Bi^{III}; E_{dep} =-1200 mV; t_{dep} = 120 s; other conditions as indicated in item 2.3.

Dissolved oxygen have been known to affect stripping response of heavy metals determined on *in situ* MFE. Figure 2 indicated an advantage of BiFE over MFE, that it may not need to deaerate analytical solution during ASV procedure for determination of Pb^{II} and so that it allowed to reduce analytical time.

Influence of zinc, cadmium and copper

Heavy metals (Zn, Cd and Cu) usually accompanies with lead in environmental samples. They (especially Cu) were found to influence lead stripping response in ASV procedure on BiFE (Wang et al., 2000,2001). Our previous study (Hop et al., 2003) and this study shown that:

- Lead peak current decreased greatly (20 – 50%) with increase in Cu^{II}/Pb^{II} ratio (ppb/ppb) between 2/1 and 5/1;
- Zn and Cd insignificantly affected lead stripping response: lead peak current decreased over 20% when the ratio (ppb/ppb) of Zn^{II}/Pb^{II} and Cd^{II}/Pb^{II} higher than 50/1.

Although the heavy metals affected lead stripping response, linear correlation between lead peak current and lead concentration on *in situ* BiFE was still good ($R \geq 0.99$). In addition, level of each metal (zinc, cadmium and copper) are usually not so much higher than lead level in blood and urine samples. Therefore, *in situ* BiFE can be used for ASV determination of lead in the samples.

3.2. Sensitivity, reproducibility, detection limit and linear range

Under suitable conditions (as indicated in item 2.3), the DP-ASV with *in situ* BiFE for lead gained high sensitivity and low detection limit (3σ): 150 – 200 nA/ppb and 0.7 ppb, respectively. Reproducibility of stripping peak current of lead on *in situ* BiFE was good (RSD < 7%, n = 20). Linearity was good (Figure 3) in the range of $2 \div 100$ ppb Pb^{II} (R = 0.999).

3.3. Analytical application

Precision: Precision of the DP-ASV with *in situ* BiFE and GF-AAS for lead was checked by replicate analysis of several blood and urine samples selected randomly from all the samples collected. The results obtained (table 1) shown that precision of both method was good with RSD < 4.5%.

Accuracy: Accuracy of the DP-ASV and GF-AAS for lead was checked by analysis of blood and urine samples spiked (Table 1). In addition, accuracy of the DP-ASV was assessed by comparison with the GF-AAS.

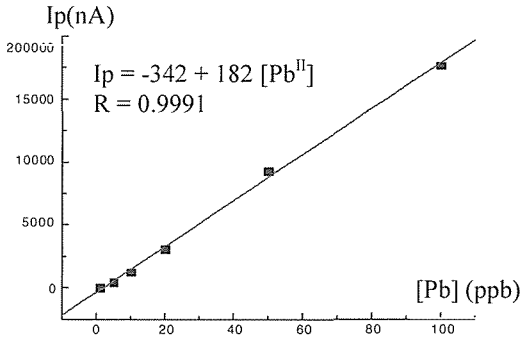


Figure 3. Linear correlation between lead peak current and lead concentration.
Conditions: as indicated in item 2.3.

Table 1. Precision and accuracy of the DP-ASV and GF-AAS for Pb^{II} in blood and urine samples

No	Sample[a]	DP-ASV				GF-AAS			
		Pb^{II} in sample, µg/dL	RSD (%)	Pb^{II} in sample spiked [b], µg/dL	Recovery (%)	Pb^{II} in sample, µg/dL	RSD (%)	Pb^{II} in sample spiked [b], µg/dL	Recovery (%)
1	B6-1	15.57; 15.58 Mean = 15.6	0.04 (n =2)	20.5	99.5	15.7	-	-	-
2	B6-2	45.70; 45.71 Mean = 45.7	0.01 (n =2)	51.3	101.2	45.7	-	-	-
3	B9-1	46.7	-	-	-	45.1; 46.5; 45.4; Mean = 45.7	1.7 (n = 3)	-	-
4	B10-1	30.12; 28.28 Mean 29.2	4.5 (n =2)	33.3	97.4	28.3	-	-	-
5	B10-2	11.2	-	-	-	-	-	16.4	100.6
6	Bc23-1	20.1	-	-	-	15.2	-	-	-
7	Bc23-2	12.7	-	-	-	12.9; 12.6; 12.5; Mean = 12.7	1.5 (n = 3)	17.7	100
8	U6-2	13.4	-	-	-	8.4; 8.6; 8.3 Mean = 8.4	2.3 (n = 3)	13.2	98.0
9	U9-2	10.0	-	-	-	8.3	-	-	-
10	Uc23-2	11.6	-	-	-	12.9; 12.9; 13.2 Mean = 13.0	1.5 (n = 3)	17.9	99.7

[a] B and U: blood and urine sample of the suspected group; Bc and Uc: blood and urine sample of the control group; the first number indicates order of sample; the second number indicates order of sampling session.

[b] each sample (blood or urine sample) was spiked with 5 ppb Pb^{II}.

Accuracy of the DP-ASV was good with recovery from 98.0 to 100.6%. Pair test (Miller, 1988) used for the two methods (DP-ASV and GF-AAS) shown that the difference of lead concentration between the two methods was statistically insignificant ($p > 0.05$). In other words, the DP-ASV had good accuracy, accepting that the GF-AAS was a validated analysis measurement of lead.

Assessment of blood and urine lead level

Blood and urine lead was determined by DP-ASV using *in situ* BiFE (Table 2). Quantitation of lead was made by standard addition method (Figure 4).

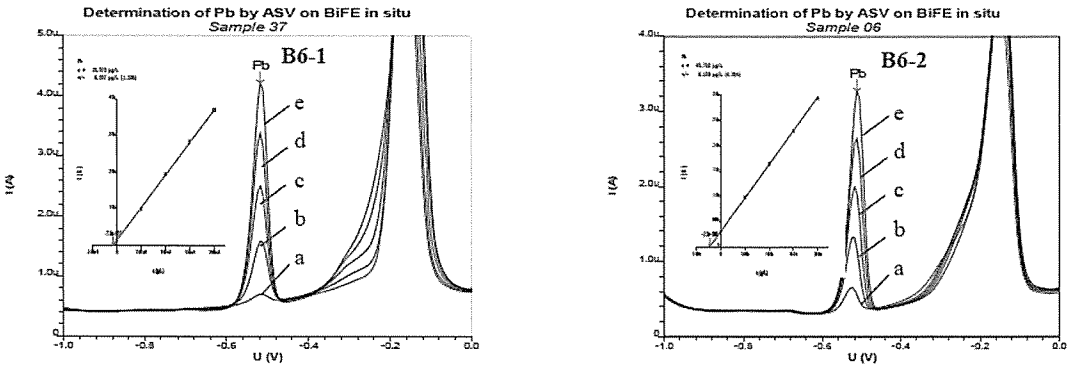


Figure 4. Lead stripping voltammograms recorded for DP-ASV determination of lead in 2 blood samples (B6-1 and B6-2): a. sample; b, c, d, e. standard additions, each 5 ppb Pb^{II} .
Conditions: as indicated in item 2.3.

Table 2. Lead concentration found in blood and urine samples taken from the residents at Canh Duong village

Sample	Study group	Min – Max (µg/dL - µg/dL)	Mean (µg/dL)	Median (µg/dL)	Standard deviation (µg/dL)	Variation Coefficient (%)
Blood	Suspected group (n = 30)	5.9 – 118.9	34.7	24.7	28.2	81.3
	Control group (n = 10)	8.0 – 25.7	16.3	16.7	5.1	31.2
Urine	Suspected group (n = 11)	5.0 – 21.8	12.9	10.0	6.0	46.5
	Control group (n = 4)	8.5 – 13.1	10.6	10.5	2.1	19.8

Difference of blood lead levels (means) between the first and second session were statistically insignificant ($p > 0.05$). However, difference of blood lead levels (means) between the suspected and control group (table 2) were statistically significant ($p < 0.05$). Blood lead level in the suspected group was 2 times higher than that in the control group. Blood lead levels in 11 out of 30 samples (36.6%) of the suspected group were higher than 30 µg/dL, a level recommended to make clinical intervention (Goldfrank's, 2002). Especially, 6 samples of the suspected group had blood lead

higher than 50 μg/dL. This level may cause brain injure and disorder in kidney function (Goldfrank's, 2002). Besides, a concern emerged that blood lead levels in 37 out of 40 samples (92.5%) of both suspected and control group were higher than that recommended by WHO (10 μg/dL).

Difference of urine lead levels (means and medians) between the suspected and control group (table 2) was statistically insignificant ($p > 0.05$). The urine lead levels of the two groups were higher than normal level (80 μg/24 h (Goldfrank's, 2002); noticing that the unit of urine lead level in table 2 was μg/dL and average urine volume was about 1 – 1.5 L/day-person). Correlation between blood lead and urine lead was not found under this study ($R = 0.24$).

The above results obtained from this preliminary study shown that practical concerns about high lead exposure appeared at the village under study, especially in the suspected group.

4. Conclusion

Bismuth – a nontoxic and environmental friendly metal can be successfully used as working electrode for ASV determination of lead in blood and urine samples. Blood lead level in the residents under study was rather high. This has caused concern about health risks not only in Canh Duong village, but also in the province. Followed-up actions to reduce lead exposure in the areas should be urgently done.

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