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Short communication

Quantitative determination of zinc in milkvetch by anodic stripping voltammetry with bismuth film electrodes

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Abstract

Bismuth film electrode (BiFE) was shown to be an attractive alternative to common mercury film electrode (MFE) for anodic stripping voltammetric measurements. In this study, bismuth film, that was in situ deposited onto glassy carbon electrode, was used to detect zinc content of milkvetch, used in traditional Chinese medicine. Variables affecting the response have been evaluated and optimized. Experimental results showed a high response, with a good linearity (between 0.5×10^{-6} mol L^{-1} and 3×10^{-6} mol L^{-1}) a good precision (R.S.D. = 3.58%) and a low detection limit (9.6×10^{-9} mol L^{-1} with a 120 s anodic). The anodic stripping performance makes the bismuth film electrode very desirable for measurements of trace nutritive element zinc in milkvetch and should impart possible restrictions on the use of mercury electrode.

Keywords: Bismuth film electrode; Anodic stripping voltammetry; Milkvetch; Nutritive element

1. Introduction

Milkvetch is one of the most important drug used in traditional Chinese medicine, and it contains lots of trace elements, such as zinc, iron and manganese, etc. It is well known that zinc, as a kind of nutritive elements, has an important role on mind, physical and immunologic function of mankind. Today accurate measurement of zinc, in food and drugs, has been paid more and more attention. Comparing to traditional analytical methods, anodic stripping voltammetry is a powerful electroanalytical technique for trace metal measurements [1]. Mercury film electrode was extensively used for stripping voltammetry analysis [2–5]. However, because of the toxicity of mercury, which is also considered responsible for environmental pollution, considerable efforts have been devoted to the investigation of alternative electrode materials. Obviously, alternative electrodes should be developed to suit the need of environment, such as chemically modified electrodes [6]. Recently, Wang et al. carried out research about environment-friendly bismuth film electrodes (BiFE) as substitute of the mercury film electrodes [7–9]. And BiFE were applied for anodic stripping voltammetric trace analysis of some metal ions, which involves in situ deposition of the bismuth film onto glassy carbon (GC) electrodes with subsequent stripping detection of the accumulated analytes [10–12]. Due to their advantages BiFE become increasingly interesting for the determination of trace metal as well as some heavy metals by stripping analysis [13–15].

In this study, we determined the optimum conditions by researching factors that affect anodic stripping voltammetry of zinc on bismuth film electrodes, and under these optimum conditions, zinc content of milkvetch was measured. Experimental results obtained by anodic stripping voltammetry were compared to those obtained by flame atomic absorption spectrometry (FASS).

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2. Experimental

2.1. Reagents and solutions

All solutions were prepared with double-distilled water. The zinc standard stock solution (1 mol L^{-1}) was obtained from Standard Center of China and diluted as required. Bismuth nitrate (analytical grade) (0.01 mol L^{-1}) and potassium cyanide (analytical grade) (1 mol L^{-1}) standard stock solutions were also obtained from Standard Center of China. Solution of 0.5 mmol L^{-1} bismuth, used for the deposition of the bismuth film electrodes was prepared by diluting the standard stock solution.

Milkvetch was obtained, respectively, from Heng mountain of Shanxi Province and Mongolia.

2.2. Preparation of the milkvetch samples

After being desiccated, 300 g of milkvetch received, respectively, from Shanxi Province and Mongolia were poached for 30 min with double-distilled water where liquid level was 2 cm above the milkvetch according to the poaching way of traditional Chinese medicine, then the operation was repeated once more. All juice was mixed together and then diluted to 250 mL. After that 25 mL of milkvetch juice was put into a 100 mL beaker, and 18 mL of a mixture of nitric acid and perchloric acid (1:3) was added and the mixed solution was nitrified by heating with electric mantle up to produce white smoke for about 3 min. Here, solution was about 10 mL, and then it was diluted to a final volume of 250 mL with double-distilled water, from which 10 mL was taken out and then 10 mL of 1.0 mol L^{-1} KSCN solution and 2.5 mL of 1.0×10^{-4} mol L^{-1} $Bi(NO_3)_3$ were added. Once more mixed solution was diluted to a definite volume of 50 mL.

2.3. Electrochemical measurements

All experiments were performed with a CV2000 electrochemical analyzer (Apparatus Factory of Dufu, Zhengzhou, China) in connection with a three-electrode cell. A saturated calomel electrode and a platinum electrode acted as reference and auxiliary electrodes, respectively. And a bismuth film coated glassy carbon (GC) electrode (3 mm diameter) served as the working electrode. Mercury film coated GC electrodes were used for comparison.

2.4. Preparation of the BiFE

Prior to its use, the glassy carbon was polished with alumina slurry and then washed under sonication for 5 min. Stripping voltammetric measurements were performed by in situ deposition of bismuth (or mercury) film and target metal after removing dissolved oxygen. A deposition potential (−1.4 V) was applied to the GC electrode while the solution was stirred, then the stirring was stopped and after a definite equilibrium time, the voltammogram was recorded. After each measurement, working electrode potential was adjusted at 0.9 V and electrodes were rinsed for 60 s in order to remove the bismuth films. All experiments were performed at $20 \pm 3\,^{\circ}C$ after removing oxygen.

2.5. Flame atomic absorption spectrometry

Flame atomic absorption spectroscopy was performed with an AA320 atomic absorption spectrophotometer (Shanghai Analytical Instrument Factory). Three hundred grams milkvetch sample was prepared as described above. After the mixed solution was nitrified by heating with electric mantle up to produce white smoke for about 3 min, we obtained about 10 mL solution, which was diluted to a definite volume of 50 mL for FAAS measurements. The absorption value of zinc was measured at 213.9 nm with hollow cathode lamp.

3. Results and discussion

3.1. Optimisation of experimental conditions for anodic stripping voltammetry for zinc determination

To get optimal conditions of anodic stripping voltammetry for zinc determination, effects of supporting electrolyte concentration, bismuth concentration, accumulation potential and time, pH were considered.

By comparing to sodium acetate buffer solution as supporting electrolyte, we found that the response of bismuth electrode presented better wave profile and higher sensitivity with KSCN as electrolyte. The effect of concentration of the supporting electrolyte KSCN, on anodic stripping voltammetry, was then examined in the range of 0.1–0.4 mol L^{-1}. We found that the response of bismuth presented better wave profile and higher sensitivity when the concentration of the supporting electrolyte KSCN was 0.2 mol L^{-1}. This concentration was used for following experiments.

The effect of Bi(III) concentration on peak current of zinc has been investigated. The concentration of the Bi(III) solution controls the thickness of the Bi film. We found that the thickness of the film did not affect the peak position of Zn, but it had effect on peak current of zinc. In Fig. 1, we can see that with increasing bismuth concentration, the peak current of zinc increased in the range of 3×10^{-6} to 5×10^{-6} mol L^{-1}, and then decreased over the concentration of 5×10^{-6} mol L^{-1}. The higher peak current is obtained for a bismuth concentration equal to 5×10^{-6} mol L^{-1}. The high concentration of Bi(III) over 5×10^{-6} mol L^{-1} may be result in multilayer deposition of Bi, which is not favorable for Bi adhesion on GC electrode surface.

In our study, peak current of zinc was larger when the accumulation potential is equal to −1.4 V. And we investigated the effect of accumulation time in the range of 0–150 s on peak current. The response of the bismuth electrode increased rapidly with the accumulation time up to 120 s, as

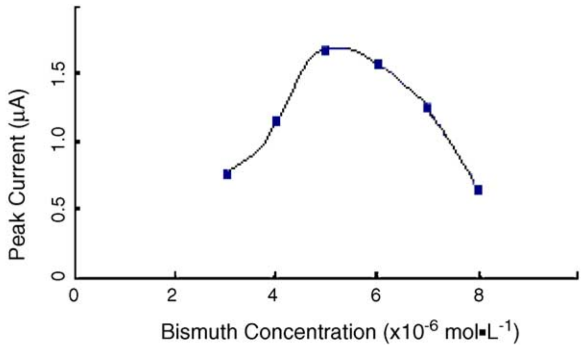

Fig. 1. The effect of Bi(III) concentration on peak current of zinc stripping voltammetry.

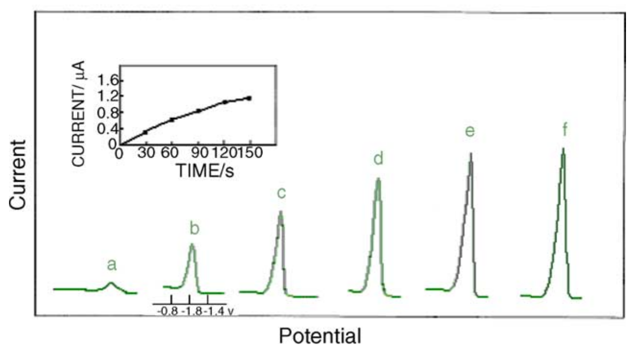

Fig. 2. Voltammogram of a 5×10^{-6} mol L^{-1} zinc solution following different accumulation times: (a) 0; (b) 30; (c) 60; (d) 90; (e) 120; (f) 150 s. Inset: the resulting plot of current vs. accumulation time.

we can see from Fig. 2; however, increased slowly over 120 s.

Effect of pH of the solution on anodic stripping response was also studied. We can see from Fig. 3 that the largest anodic stripping response was obtained for a solution pH equal to about 3.0.

Fig. 4 displays stripping current plot obtained upon increasing the zinc concentration. The six increments of 5×10^{-7} mol L^{-1} yielded a highly linear calibration plot and the equation of the linear calibration is $I = 6.2758C + 0.0677$ ($R = 0.9995$). The detection limit was estimated from the signal-to-noise ratio (S/N = 3) and it equals to of 9.6×10^{-9} mol L^{-1}. In order to check the reproducibility of the electrode, a series of 10 repetitive measurements at a 1.0×10^{-4} mol L^{-1} zinc concentration were performed with the same glassy carbon electrode, which was treated after each experiment to remove the bismuth film, and yielded a very stable and repetitive response with a relative standard deviation of 3.58%. The results showed that the BiFE has high sensitivity and good reproducibility.

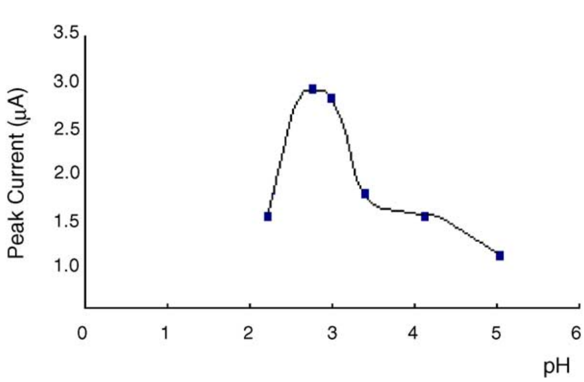

Fig. 3. pH effect on peak current.

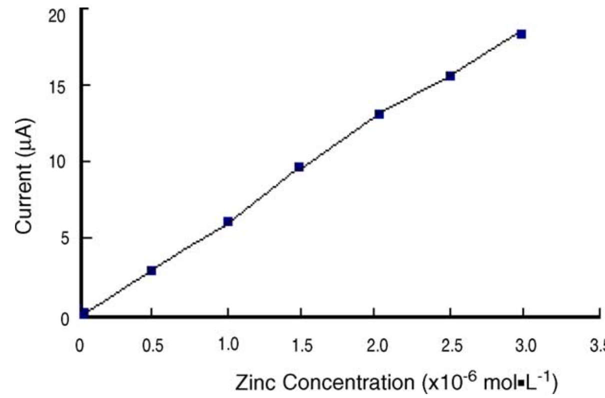

Fig. 4. Peak current dependence on zinc solution concentration.

3.2. Comparison of BiFE with MFE

Anodic stripping measurements of zinc are commonly carried out at mercury film electrodes. Here we compared the anodic stripping voltammetric response of the mercury film and bismuth film electrodes for a 10^{-4} mol L^{-1} Zn^{2+} concentration, with a 120 s accumulation. From results shown in Fig. 5, it can be concluded that bismuth electrode presents a well-defined and larger stripping peak comparing to mercury film electrode and its sensitivity is two times higher than that of mercury film electrode. This result can be attributed to the formation of zinc–bismuth alloy as opposed to metal amalgams [13], and such alloy leads to a well-defined stripping peak.

3.3. Detection of zinc content in the milkvetch

Zinc content in the milkvetch, respectively, from Shanxi Province and Mongolia were analyzed under the optimum conditions: supporting electrolyte concentration 0.2 mol L^{-1}, bismuth concentration 5×10^{-6} mol L^{-1}, accumulation potential −1.4 V, anodic time 120 s and pH 3.0. The results obtained by anodic stripping voltammetry (ASV) are in good agreement with those obtained by FASS measurements (Table 1). The results of the total zinc

Table 1
Zinc content in the milkvetch, respectively, from Shanxi Province (sample A) and Mongolia (sample B) ($n = 5$)

Sample	ASV measurements (μg/g)	FASS measurements (μg/g)
A	2.89 ± 0.10	2.81 ± 0.05
B	2.87 ± 0.10	2.78 ± 0.05

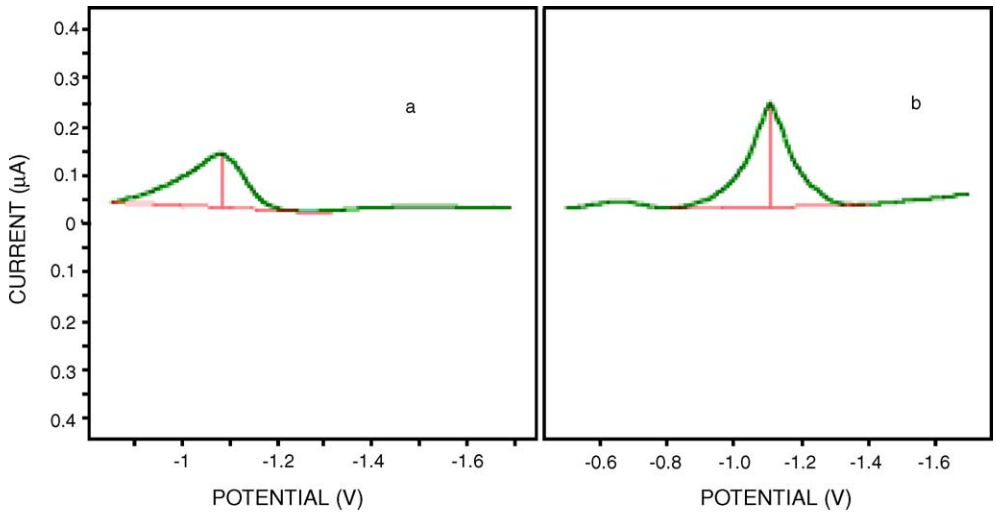

Fig. 5. Comparison of the anodic stripping voltammetric response to 10^{-4} mol L^{-1} Zn (II) after removing oxygen at the mercury film (a) and bismuth film (b) electrodes. 0.2 mol L^{-1} KSCN deaerated solution.

in Milkvetch determined by FASS and free ion or labile complex determined by ASV being equal shows that zinc is totally under the forms of a free ion or a labile complex.

4. Conclusion

We have demonstrated that bismuth film electrodes are very suitable for anodic stripping measurements of trace zinc as a substitute of noxious mercury film electrodes. BiFE can hopefully expand its scope and application on measurements of other trace metal elements in other matrices used in traditional Chinese medicine.

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References

[1] J. Wang, Stripping Analysis, VCH, Publishers, Deerfield Beach, 1985.
[2] A.M. Bond, Anal. Chim. Acta 400 (1999) 333.
[3] F.L. Coco, P. Monotti, V. Fiecchi, L. Ceccon, Anal. Chim. Acta 409 (2000) 93.
[4] E. Fischer, C.M.G. van den Berg, Anal. Chim. Acta 385 (1999) 273.
[5] O.A. Farghaly, Microchem. J. 75 (2003) 119.
[6] Y. Bai, S. Li, Y. Zhou, J. Mo, M. Li, Prog. Electroanal. Chem. (1999) 242.
[7] J. Wang, J. Lu, S.B. Hocevar, P.A.M. Farias, B. Ogorevc, Anal. Chem. 72 (2000) 3218.
[8] J. Wang, J. Lu, Electrochem. Commun. 2 (2000) 390.
[9] E.A. Hutton, B. Ogorevc, S.B. Hocevar, F. Weldon, M.R. Smyth, J. Wang, Electrochem. Commun. 3 (2001) 707.
[10] J. Wang, J. Lu, Ü.A. Kirgöz, S.B. Hocevar, B. Ogorevc, Anal. Chim. Acta 434 (2001) 29.
[11] A. Królicka, A. Bobrowski, Electrochem. Commun. 6 (2003) 99.
[12] G. Kefala, A. Economou, A. Voulgaropoulos, M. Sofoniou, Talanta 61 (2003) 603.
[13] A.T. Maghasi, H.B. Halsall, W.R. Heineman, H.L. Rodriguez Rilo, Anal. Biochem. 326 (2004) 183.
[14] E.A. Hutton, S.B. Hocevar, B. Ogorevc, M.R. Smyth, Electrochem. Commun. 5 (2003) 765.
[15] K. Vytřas, I. Švancara, R. Metelka, Electroanalysis 14 (2002) 1359.