J. Mater. Environ. Sci. 3 (1) (2012) 85-90 *Ghanjaoui et al.*
ISSN : 2028-2508
CODEN: JMESCN

Fast procedure for lead determination in alcoholic beverages

M. E. Ghanjaoui*, M. Srij, M. Hor, F. Serdaoui, M. El Rhazi
Laboratory of Electrochemistry and Physical Chemistry, Faculty of Sciences and Technologies, Mohammedia, Morocco

Received in 19 June 2011, Revised 19 Sept 2011, Accepted 19 Sept 2011.
*Corresponding Author:- Email: ghanjaoui2000@hotmail.com , Tel: +212 675 579 577

Abstract

In this paper, the system based on Bismuth Film Electrodes BiFEs combined with rotating disk electrode (RDE) was applied to determine lead in beer samples. Lead and bismuth were simultaneously deposited by reduction at -1V on a rotating carbon-paste disk electrode. Then, the preconcentrated metals were oxidized by scanning the potential of the electrode from -1 to -0.4V using a square-wave waveform. The electrode displayed excellent linear behavior in the examined concentration range, from 5 to 85 µg.L^{-1} lead (r^2=0.998). Finally, the proposed method (Square-Wave Anodic Striping Voltammetry (SWASV)) was applied for determination of lead in beer. Beer samples were digested with dry ashing and wet ashing procedures. The wet ashing procedure was chosen for the digestion of all the beer samples because it required shorter time. The present results were validated by Inductively Coupled Plasma Atomic Emission Spectroscopy ICP-AES.

Keywords: BiFE, RDE, SWASV, Alcoholic beverages.

Introduction

Toxic effects of the minerals pollutants in Alcoholic beverages may have an additive effect to induction of alcoholism. A typical example is the presence of lead in wines **[1]**. Several investigators have shown that an accumulation of lead in mitochondria of mice occurs with the simultaneous ingestion of small doses of lead **[2]**. The common analytical methods used for heavy metals determination include atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), inductively coupled plasma–optical emission spectrometry **[3-6]** and ion chromatography is also used for the analysis of metals, for example in vodka **[6, 7]**.

Electrochemical stripping analysis has been widely recognized as a powerful tool for determination trace metals in alcoholic beverages samples **[8 - 12]**. Its remarkable sensitivity is attributed to the combination of an effective preconcentration step with advanced electrochemical measurements of the accumulated analytes.

The application of carbon paste electrodes CPEs in analytical chemistry has attracted considerable attention in recent years. CPEs have several advantages such as non-toxic, low background current, wide range of used potential, rapid renewal, and easy fabrication **[13]**. The rotating-disk electrode is a famous system responsible of mass transport control, leading to high sensitivity. Some electroanalytical studies involving modified electrodes in hydrodynamic configurations have been reported in the literature for analytical purposes **[14, 15]**.

Mercury film electrodes (MFE's) and the hanging mercury drop electrode (HMDE) **[16, 17]** have been traditionally used for ASV owing to the advantageous analytical properties of mercury in the negative potential range. However, the increased risks associated with the use, manipulation and disposal of metallic mercury or mercury salts have led some countries to completely ban mercury. Following this general trend for more environmentally-friendly analytical methods, alternative electrode materials are continuously been sought. Recently, bismuth film electrodes (BiFE) have drawn considerable interests due to its remarkable low toxicity and its ability to form alloy with many metals, as well as its partial insensitivity to dissolved oxygen

[14, 18-30], but most of the earlier work on BiFEs was concerned with insights into their fundamental properties. However, its application to environment, clinical, and food analysis was still rather limited and immature.

In the last few years, our group has reported several studies of minerals elements analysis based on modified electrode by conducting polymers or by metallic films **[31-33]**. In this work, we performed a thorough study of the parameters affecting the electrochemical behavior of BiFE to achieve high sensitivity for determination of Pb^{2+} in alcoholic beverages.

2. Materials and methods

2.1. Apparatus

Voltammetric measurements were performed using an AUTOLAB PGSTAT 10 Potentiostat (Ecochimie, Utrecht, Netherlands) controlled by GPES 4.8 software. The three electrode system consists of the rotating disk electrode controlled by oxford motor (0,0707cm^2) as working electrode, Saturated Electrode Calomel (SEC) as the reference electrode and platinum wire as the counter electrode. The pH was adjusted using a Fisher Sientific Accumet AB15 BASIC pH meter. Analysis ICP-AES were carried out using an Ultima 2 Jobin Yvon Model spectrometer.

2.2. Chemicals and sample preparation

The chemicals reagent used in the preparation of stock solutions were of analytical reagent grade. All solutions were diluted by distilled water. Stock of acetate buffer (1M) was prepared by Acetic acid CH_3COOH (**Fisher**) and Sodium Acetate CH_3COONa (**Breckland Scientific**). Stock solutions for in situ bismuth plating, were prepared from Bi $(NO_3)_3$ (**Riedel-Dehaen**), while Pb $(NO_3)_2$ (**Riedel-Dehaen**) were employed in the preparation of metal ion stock solutions in 1000 µg/l concentrations.

2.3. Procedure

2.3.1. Bismuth film electrode substrates: carbon paste electrodes

The carbon paste used was prepared by intimate hand mixing of 1 g graphite powder and 0, 3 ml of paraffin oil until a uniformly wetted paste was obtained. The paste was then inserted into the electrode cavity. A stainless steel wire provided the electrical contacts, the electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode Before each use of Carbone Paste Electrode (CPE), it was rubbed with a piece of paper until a smooth surface was observed.

In situ bismuth films were prepared by spiking the sample with the required Bi^{3+} concentration in the beginning of each set of experiments. Following that, increasing metal ion concentrations were studied by incremental spiking of the sample with the appropriate volume of Pb^{2+} stock solution.

2.3.2. Preparation of real sample

In this study, six beer samples purchased from local supermarket were analysed. For the determination of lead by the proposed method in beer, two methods were used.

2.3.2.1. Wet-ashing method

Wet-digestion of beer was performed using an oxi-acidic mixture of 5ml HNO_3 (67%) and 5ml of H_2O_2 (37%) for 25ml of sample. This mixture was heated until all the organic matter was destroyed. The final solution was transferred to a 50 ml volumetric flask. After that, 5 ml of acetate buffer (1M) and 2.5 ml of bismuth solution (10000µg.L^{-1}) were added. pH of mixture was adjusted at 4.5 and diluted with distilled water until 50 mL.

2.3.2.2. Dry ashing method

Beer samples were submitted to degasification by heating reflux during 40 min under 120 °C. After that, 5±0.5 g of sample was placed in a high form porcelain crucible. The furnace temperature was slowly increased from room temperature to 550 °C in 1 h. The samples were ashed for about 24 h until a white ash residue was obtained. The residue was dissolved in 5 ml of HNO_3 (25% v/v) and the mixture, when necessary, was heated slowly to dissolve the residue. The solution was transferred to a 50 ml volumetric flask. The 5 ml of Acetate buffer (1M) and 2.5 ml of bismuth solution (10000µg.L^{-1}) were added. pH of mixture was adjusted at 4.5 and diluted with distilled water until 50 mL.

2.3.3. Real sample analysis

Because of complexity of matrix, the lead contents was always determined by the multiple standard addition method, each data point used was the average of at least for three distinct measurements.

3. Results and discussion

3.1. Procedure for lead determination by SWASV method

All measurements were carried out in 0.1M acetate buffer (pH 4.5) containing 500 µg.L^{-1} of bismuth (All parameter used for lead determination are given in **table 1**). Bismuth films were prepared by spiking the sample with 500 µg.L^{-1} Bi(III) and depositing bismuth on the surface of the electrode at -1V (vs. SCE) under rotation of the electrode disk for a carefully defined period of time. Then, the electrode rotation was stopped, followed by 15 s of equilibration. The voltammograms were recorded by applying a positive potential scan from -1 to -0.4V (with a step increment of 5mV and amplitude of 25 mV). A 30s conditioning step at +0.3V (under rotating of electrode disk) was used to remove the target of bismuth film prior to the next cycle. After recording the background voltammograms in 0.1M acetate buffer (pH 4.5) containing 500 µg.L^{-1} of bismuth, lead solution was added to the cell as required and in situ mode of deposition was started by simultaneous preconcentration of bismuth and lead. The measurements were repeated three times. Finally, our method was validated by mean of ICP-AES. All experiments were performed at room temperature.

3.2. Calibration curve

Using the chosen optimised condition presented in **table 1, Fig. 1** show the calibration curve for concentration ranging from 5 to 85µg/l, and **table 2** shows the characteristics of calibration graph for lead. The limit of detection (LOD) was calculated as the concentration corresponding to signals equal to three-times the standard deviation of five measurements.

Table 1: Square Wave Anodic Striping Voltammetry parameters

Parameters	Values
Conditioning potential	+0.3V
Conditioning time	30s
Deposition potential	-1V
Deposition time	120s
Rotation speed	500rpm
Equilibrium time	15s
Sweep potential	[-1 to -0.4V]
Amplitude	25 mV
Frequency	25 Hz
Step potential	5 mV

Table 2: Calibration curve parameters

Parameter	Calibration
Calibration range(µg.L^{-1})	5 – 85
Equation	$y = 0.28x + 0.4$
r^2	0.998
RSD (n=5)	3.4%
Detection limit (µg.L^{-1})	0.27

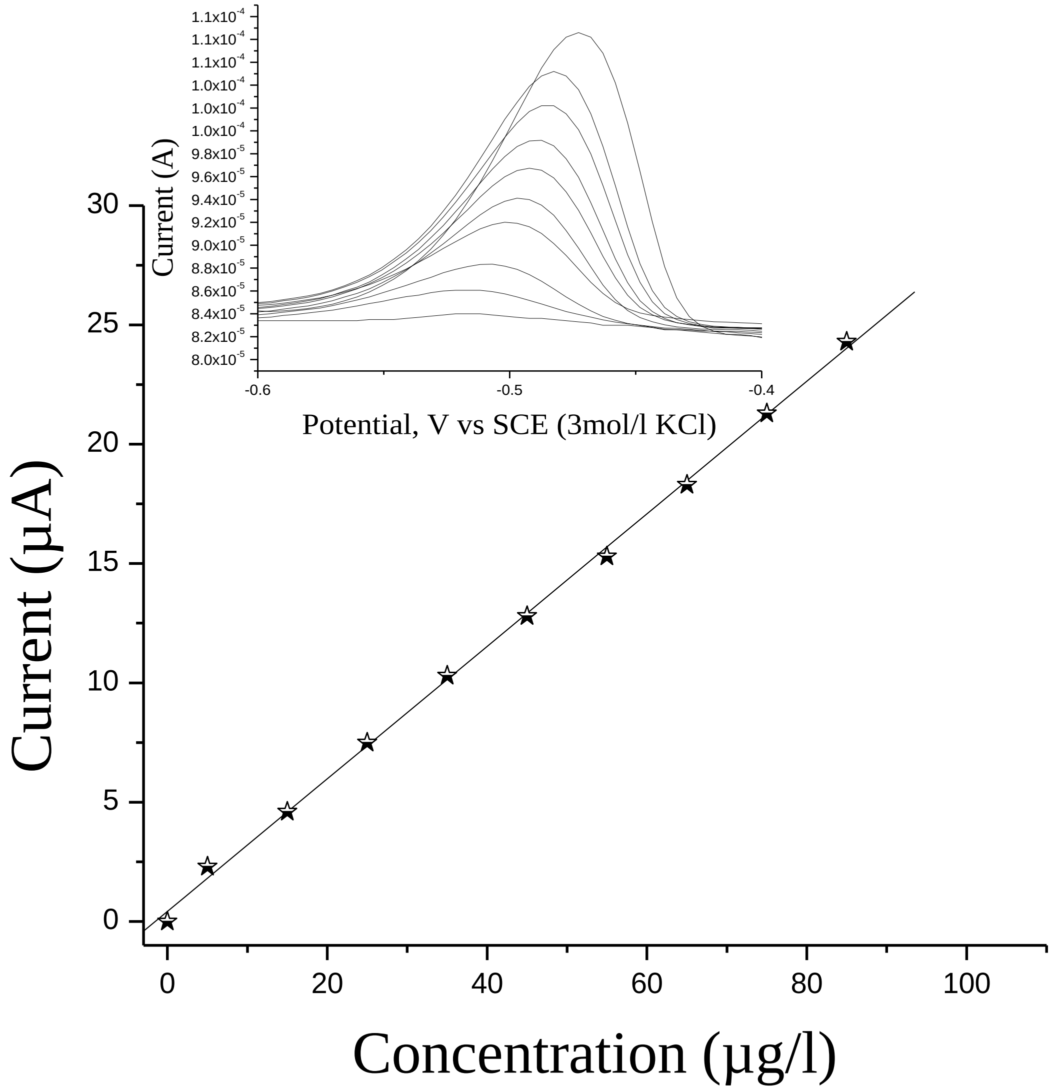

Figure 1: Calibration curves for lead in 0.1M acetate buffer (pH 4.5) containing 500 µg.L^{-1}of bismuth. Lead was ranged from 5 to 85µg.L^{-1}.

Reproducibility of the response of the BiFE was determined at five different electrodes emerged in solution containing 50µg.L^{-1} of lead, the %R.S.D value of lead is in order of 3.4%.

3.3. Determination of lead in beer samples

The fact that toxic metals are present in high concentrations in alcoholic beverages is of particular importance in relation to natural sources (soil, water, cereal, hops and yeast) as well as from environmental contamination, fertilisers, pesticides, industrial processing and containers **[34].** The maximum allowed concentration of lead in alcoholic beverages established by the Office International de la Vigne et du Vin (OIV) is 200µg.L^{-1}.

Under the conditions reported in paragraph 3.1. BiFEs were applied to the analysis of beer samples. These experiments demonstrated that it was possible to use SWASV on BiFE's in order to determine Pb at greatly varying concentrations by a judicious choice of the experimental conditions. In the **table 3**, the results of lead concentrations in two beer samples obtained by SWASV method using wet ashing and dry ashing pre-treatment have been presented. The simple comparison between wet ashing and dry ashing digestions methods has been realized, the present results show that the wet ashing treatment provides the same recoveries obtained for dry ashing method in a very short time.

Table 3: Results for the determination of Pb (µg.L^{-1}) in beer samples treated by Dry ashing and wet ashing digestions methods

Samples	Wet ashing	Dry ashing
S_1	92±2	89±3
S_2	127±4	120±5

Representative results for the determination of lead by SWASV method in four other samples of beer are illustrated in **Table 4** using wet ashing procedure. The lowest and highest lead levels were found to be 92 µg.L^{-1} and 280 µg.L^{-1} in all beer samples illustrated in table 3 and 4. For all samples collected in Moroccan marked, two samples per six exceeded 0.2 mg Pb/Kg (200 µg.L^{-1}) wet weight recommended by the Office International de la Vigne et du Vin (OIV). The results obtained by SWASV in table 4 are validated by ICP-AES method; the obtained recoveries were ranging from 93 to 98%. The comparative study suggests that there is satisfactory agreement between the two techniques SWASV and ICP-AES.

Table 4: Results for the determination of lead (µg.L^{-1}) in four beer samples treated by wet-ashing method, analyzed by SWASV and by ICP-AES

Samples	SWASV	ICP-AES	Recovery (%)
$\mathbf{S_3}$	112±2	120	93
$\mathbf{S_4}$	152±4	155	98
$\mathbf{S_5}$	252±7	258	96
$\mathbf{S_6}$	280±6	294	95

Conclusion

In this study, we developed a novel method to determine Pb in alcoholic beverages by Square Wave Anodique Stripping Voltammetry on a bismuth film electrode plated in situ. BiFE together with the standard addition method is certainly a valid analytical technique (good selectivity and, especially sensitivity) for lead determination. Moreover, such a technique may be certainly a good alternative to spectroscopic methods, which, in the case of determination of lead in complex matrices, needs too expensive equipment. Owing to the low toxicity of bismuth, inexpensive instrumentations, and simple operation, the methods will offer potential applications for this technique.

Acknowledgements

The authors gratefully acknowledge Mlle. OUADDARI from UATRS-CNRST (Unités d’Appui Techniques à la Recherche Scientifique – Centre National pour la Recherche Scientifique et Techniques), for his technical assistance.

References

1. Roses, O. E., Gonzalez, D. E., Lopez, C. M., Pineiro, A. E., Villaamil, E. C., *Bull. Environ. Contam. Toxicol.* 59 (1997) 210.
2. Fowler, B.A., Mahaffey, M.R., *Environmental health Perspectives* 25 (1978) 87.
3. Camean, A.M., Moreno, I., Lopez-Artiguez, M., Repetto, M. and Gonzalez, A. G., *Talanta* 54 (2001) 53.
4. Fiket, Ž., Mikac, N., Kniewald, G., Food Chemistry 126 (2011) 941.
5. Rodrigues, S.M., Otero, M., Alves, A.A., Coimbra, J., Coimbra, M.A., Pereira, E., Duarte, A. C., J. Food Composition and Analysis 24 (2011) 548.
6. Dugo, G., La Pera, L., Pellicanó, T. M., Bella, G. D. and D’Imperio, M., Food Chemistry 91 (2005) 355.
7. Moreira, C. M., Duarte, F. A., Lebherz, J., Pozebon, D., Flores, E. M.M., Dressler, V. L., Food Chemistry 126 (2011) 1406.

8. Jagner, D., Westerlund, S. J., Fresenius J. Anal. Chem. 117 (1980) 159.
9. Clark, A. C. and Scollary, G. R., Analytica Chimica Acta 413 (2000) 25.
10. Mikkelsen, Ø. and Schrøder, K. H., Analytica Chimica Acta 458 (2002) 249.
11. Salvo, F., Pera, L. L., Bella, G. D., Nicotina, M. and Dugo, G., Journal of Agricultural and Food Chemistry 51 (2003) 1090.
12. Brainina, K. Z., Stozhko, N. Y., Belysheva, G. M., Nzhevatova, O. V., Kolyadina, L. I., Cremisini, C. & Galletti, M., Analytica Chimica Acta, 514 (2004) 227.
13. Almeida, C. M. V. B. and Giannetti, B.F., Electrochemistry Communications 4 (2002) 985.
14. Kefala, G., Economou, A., Voulgaropoulos, A. and Sofoniou, M., Talanta 61 (2003) 603.
15. Morfobos, M., Economou, A. and Voulgaropoulos, A., Analytica Chimica Acta 519 (2004) 57.
16. Valenta, P., Mart, L. and Rützel, H., Journal of Electroanalytical chemistry 82 (1977) 327.
17. Vidal, J. C., Cepria, G., Castillo, J. R., Analytica Chimica Acta 259 (1992) 129.
18. Krolicka, A., Pauliukaite, R., Svancara, I., Metelka, R., Bobrowski, A., Norkus, E., Kalcher K., Vytras K., Electrochemistry Communications 4 (2002) 193.
19. Hutton, E. A., Ogorevc, B., Hocevar, S. B., Weldon, F., Smyth, M. R., Wang, J., Electrochemistry Communications 3 (2001) 707.
20. Hutton, E. A., Hocevar, S. B., Ogorevc, B. and Smyth, M. R., Electrochemistry Communications 5 (2003) 765.
21. Hutton, E. A., Elteren, J. T. V., Ogorevc, B. and Smyth, M. R., Talanta 63 (2004) 849.
22. Hutton, E. A., Ogorevc, B., Hocevar, S. B., and Smyth, M. R., Analytica Chimica Acta 557 (2006) 57.
23. Hutton, E. A., Hocevar, S. B., Ogorevc, B., Analytica Chimica Acta 537 (2005) 285.
24. Demetriades, D., Economou, A. and Voulgaropoulos, A., Analytica Chimica Acta, 519 (2004) 167.
25. Economou, A., Trends in Analytical Chemistry 24 (2005) 334.
26. Baldrianova, L., Svancara, I. and Sotiropoulos, S., Analytica Chimica Acta, 599 (2007) 249.
27. Cao, L., Jia, J. and Wang, Z., Electrochimica Acta 53 (2008) 2177.
28. Adraoui, I., El Rhazi, M. and Amine, A., Analytical letters 40 (2007) 349.
29. Hwanga, G. H., Han, W. K., Park, J. S., Kang, S. G., Talanta 76 (2008) 301.
30. Ghanjaoui, M.E., Srij, M., El Rhazi, M., Analytical Letters 42 (2009) 1294.
31. Majid, S., El Rhazi, M., Amine, A., Curulli, A. and Palleschi, G., Mikcrochimica acta 143 (2003) 195.
32. Adraoui , I., El Rhazi , M., Amine , A., Idrissi, L., Curulli , A. and Palleschi, G., Electroanalysis 17 (2005) 685.
33. Coulibaly, M., Ghanjaoui, M.E., Gonzalvez, A., De La Guardia, M., El Rhazi, M., Arabian J. Chem. 1 (2008) 307.
34. Yongtao, L., Van Loon, J. C. and Barefoot, R. R., Fresenius journal of analytical chemistry 345 (1993) 467.

(2012) ; http://www.jmaterenvironsci.com