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Bismuth electrodes, an alternative in stripping voltammetry

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Abstract. The heavy metals are known as highly toxic contaminants, the processes carried out in industry contribute that finally they remain dispersed in effluents and sewage, doing part of the food chain. The importance of controlling the levels of these heavy metals has become an international policy, so it has generated interest in developing new analytical methodologies for its determination [1, 2, 3, 4]. The stripping voltammetry has been considered as a family of electro-sensitive analytical techniques useful for the determination of trace levels of many metals in environmental, clinical and industrial samples [3, 4]. This work presents an overview of these bismuth-based electrodes which were introduced around 2000, which have interesting characteristics for detection of heavy metals and which represent an alternative to mercury electrodes.

1. Introduction

In the last years, the industrialization has come accompanied by different processes, which lead that the heavy metals remain finely dispersed in water, air and soil, as part of the our food chain [1]. Although there are methods with adequate sensitivity for the determination of heavy metals such as atomic absorption, atomic emission spectrometry and *ICP-MS*, electrochemical methods are one of the most favorable techniques for determination of heavy metal ions because of their low cost and high sensitivity [5]. In analytical chemistry, Anodic Stripping Voltammetry techniques (ASV) are a promising alternative to spectroscopic analysis techniques, particularly by their high sensitivity "ppb" in the detection of the elements trace in fluid and that the sensors are easily coupled to field units in addition of its low cost, low volume of reagents consumed and can be reused for several measures [6]. In this area, the potentiometric sensors represent a very interesting area and with expansion, their great development and acceptance is due to its high sensitivity and the ability to make direct measurements or act as indicators electrodes in valuation, such measures are no affected by the color or turbidity of the sample or analysis solution [7, 8, 9].

2. Results

Although mercury electrodes have been widely used for this type of electrochemical techniques because of its high reproducibility and sensitivity [9], its toxicity makes it less and less popular [3, 9, 10, 11, 12]. Different studies have been assigned to the construction of electrochemical



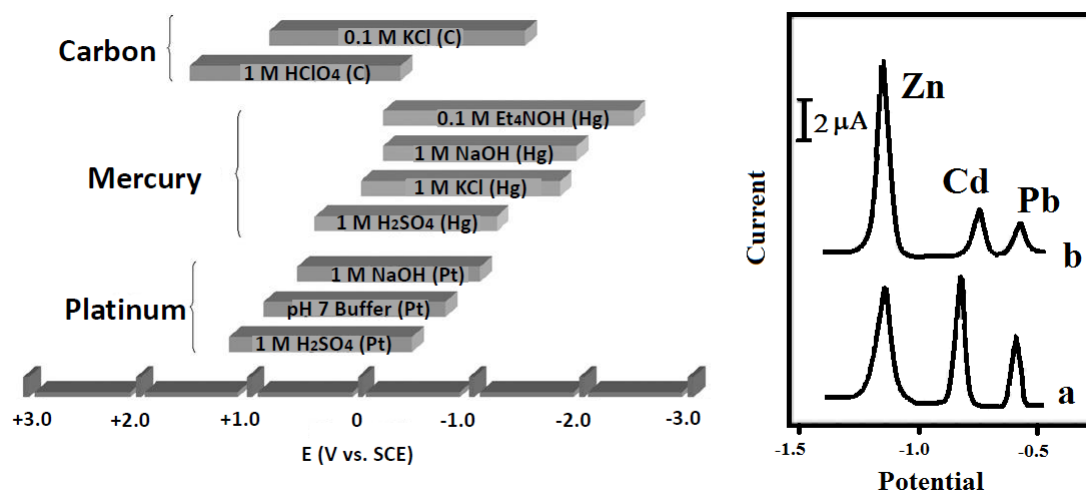


Figure 1. (Left) Behaviour potential windows for different materials. (Right) Current peaks of Cd, Zn and Pb for voltammetry. a) Bismuth electrode b) Mercury electrode (14).

sensors that do not contain mercury, a variety of different materials have been suggested and explored to produce electrodes of work for this purpose, such as noble metals (*Pt, Pd, Au, Ag*) and other metals (*Ru, Cu, Co, Ni, Pb, Sb, Bi, Al*) [7, 13]. However, bismuth is chosen due to its low toxicity [3, 9, 11, 14, 15] wide potential window and ability to form alloys with different metals [9, 10, 16, 17]. This physical-chemical behavior allows its use in the simultaneous detection of multiple electro-active species present in the same sample.

3. Bismuth electrodes in stripping voltammetry

The stripping voltammetry has been considered as a family of electroanalytical techniques more sensitive and useful for determining the level of trace metals in many samples of environmental origin, clinical and industrial, as well as organic components. The risk associated with mercury electrodes is their use, handling and disposal of waste because of its toxicity, this situation generated different researches to overcome these drawbacks; so, around 2000 the electrodes BiFEs (Bismuth Film Electrodes) were introduced, they are fabricated of a bismuth layer deposited on a suitable substrate [3, 4], different materials have been used as electrode substrate such as carbon, glassy carbon, carbon fibers, carbon paste, graphite, graphite impregnated with wax, gold, platinum [10, 16]. These Bismuth electrodes are a promise for replacing the mercury electrodes in stripping voltammetry, as well as their low toxicity, the BiFEs have shown to have electro-analytical properties similar to the mercury electrodes, such as their wide potential window, in addition to its ability to form alloys with various metals, their partial insensitivity to dissolved oxygen, their signals well defined and simple preparation [3]. The current peaks obtained at the voltammograms when uses bismuth electrodes tend to be sharp and well defined [14], in figure (1, right), which enables the identification and quantification of the metals present in the water to reliably way, quickly and economic, could be performed even in the same site where we take the sample. In recent years, different types of modified bismuth and bismuth electrodes have been developed showing a behavior comparable to MFEs (Mercury Film Electrodes) in ASV, reported methods for preparing electrodes with an active surface of bismuth have been fabricated by modifying of volume the surface of the solid electrode with metallic bismuth such as mixtures of powders of bismuth, bismuth oxide and carbon [14, 18], thermal evaporation [19], sputtering [4, 11] and electro-deposits compound Bi (III) both ex situ [10, 12, 20, 21] as in situ [9, 10, 17, 15, 21, 22, 23, 24, 25] in a conductive material. The

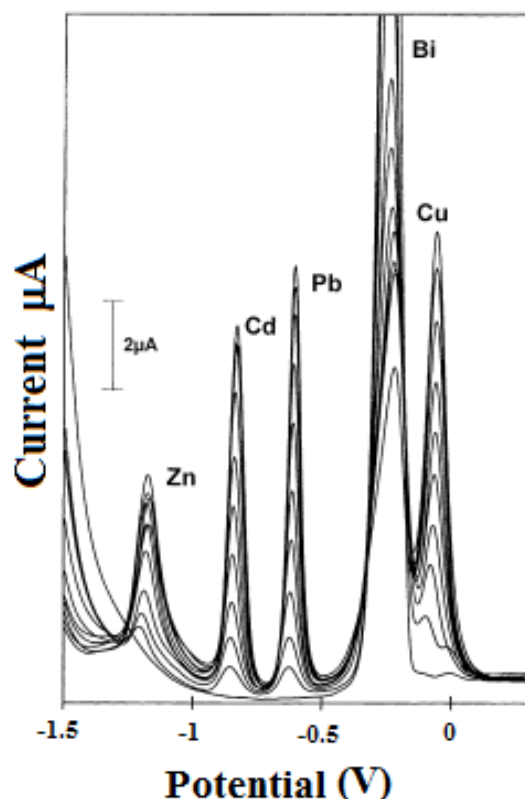


Figure 2. Square-wave stripping voltammograms for increasing concentration of copper, lead, cadmium and copper (21).

method most widely used for the preparation of BiFEs is electrochemical performed by static potentiometry (in situ or ex situ) and occasionally, by galvanostatic method, cyclic potential or pulse amperometry. However deposits by electrochemical means involving the use of salts of Bi (III), which can complicate experimental procedures and requires a conductive substrate [3, 4]. There are several reports in the literature of bismuth based electrodes were tested for the determination of trace metal ions and occasionally for the detection of organic compounds using voltammetric techniques in various forms. Some of the metals that have been reported so far include *Cd, Pb, Zn, Tl, In, CuNi, Co, Fe, Al, Mo, V, Ti, U* and *Cr* [10, 26]. Furthermore, metals have been detected in trace amounts in a variety of biological samples (hair, urine and blood) [10, 26] and environmental samples (air, tap water, sea water, river water, drains and water soils) [7, 14, 16], foodstuffs (tea, cabbage, celery, spinach, wine and tomato sauce) [7, 10, 14, 15] and Petrol [7].

4. Conclusions

In the last decade, bismuth electrodes manufactured by different methods and due to their physico-chemical Characteristics are a promise for stripping voltammetry in the determination of heavy metals especially, these electrodes are bringing us more and more to the determination of a single digit ppb of these elements, which in most cases are the limits permitted by international health organization for human consumption.

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