ISSN : 0974 - 7540 Volume 3 Issue 3

Trade Science Inc.

Research & Reviews In Electrochemistry Review

RREC, 3(3), 2012 [90-93]

# Bismuth electrode : An extremely promising alternative to electrochemical stripping analysis

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*Received: 16th June, 2011 ; Accepted: 16th July, 2011*

## ABSTRACT

Mercury electrode has been widely used in electrochemical stripping analysis of trace metals due to its high sensitivity, reproducibility, and renewability. However, due to the toxicity of mercury, alternative (environmentally friendly) electrode materials are highly desirable for both centralized and field applications. Recently, bismuth electrodes are introduced which can offer a very attractive alternative to commonly used mercury electrodes in stripping analysis. This article reviews the recent development, behaviour, scope and prospects of bismuth electrodes for stripping-based electrochemical measurements of trace metals.



## KEYWORDS

Stripping voltammetry;
Bismuth electrodes;
Mercury;
Adsorptive stripping voltammetry;
Trace metals;
Preconcentration.

## INTRODUCTION

Electrochemical stripping analysis in combination with a variety of electrodes is widely recognised as one of the most powerful analytical tools in modern trace and ultratrace chemical analysis[1]. For measurement of trace amount of toxic metals in particular, stripping analysis has frequently been referred to as the method of choice. Both Cathodic Stripping Voltammetry (CSV) and Anodic Stripping Voltammetry (ASV) offer powerful tools for the detection of trace levels of metals and impurities and these techniques are based on the amplification of the analytical response by a pre-accumulation/preconcentration step. Stripping voltammetry is a powerful electroanalytical technique for the detection of trace amount of metals in the range of ppb (parts per billion). Its high sensitivity can be attributed to the preconcentration step, during which the target metals are accumulated/deposited on to the working electrode. It is also well established and clear that, specifically due to a built-in preconcentration capability, an appropriate electrode (material or coating) plays a key role in these analyses. Proper choice of the working electrode is crucial for the success of the stripping analysis. The ideal working electrode should offer effective preconcentration, a favourable redox reaction of the target metal, reproducible and renewable surface, and a low background current over a wide potential range.

Mercury has been the electrode material of choice for many stripping applications for decades due to several electrochemical advantages such as high sensitivity, reproducibility, and renewability of the surfaces. Two basic electrode systems, the mercury film electrode (MFE) and hanging mercury drop electrode (HMDE), have gained wide acceptance in the development of anodic stripping voltammetry (ASV)[1-3]. While these small-volume mercury electrodes offer an attractive stripping performance, new alternative electrode materials with a similar performance are urgently needed for addressing growing concerns regarding the toxicity, handling, volatility, and disposal of mercury. Future regulations and occupational health considerations may severely limit (and even ban) the use of mercury as an electrode material. Such concerns regarding the toxicity of mercury (Hg) electrodes are particularly important in view of the growing demands for on-site environmental analysis and decentralized clinical metal testing.

As a consequence, immense interest has been expressed in finding new useful electrode materials and coatings in order to replace mercury. Different bare carbon, gold, silver or iridium electrodes have been used as possible alternatives to mercury[4-6]. While offering useful stripping signals for several metals, the overall performance of these non-mercury electrodes has not approached that of mercury ones, due to a low cathodic potential limit, multiple distorted (multiple/broad) peaks, large background contributions, or poor precision and resolution. The low capacitive current, large potential window and high stability, sensitivity and a low detection limit of boron-doped diamond (BDD) electrodes can be utilized for electroanalysis especially in stripping analysis of trace toxic metals[7, 8]. Although, it can not directly replace all existing mercury based electroanalytical processes, BDD materials have been shown to provide new dimension into Hg free analysis. It has been shown that BDD is much better electrode material compared to other traditional electrode materials. However, despite the several benefits of BDD electrodes, they have not found wide industrial applications, mainly due to their high cost and the difficulties to find a suitable substrate for the deposition of thin diamond films. Hence, the development of reliable non-mercury electrodes is considered a major challenge for stripping analysis in the early stage of the 21st century.

Bismuth (Bi) is an environmentally-friendly element, with very low toxicity, and a widespread pharmaceutical use[9]. The development and use of green electrode materials is extremely attractive for the routine use of disposable (one-shot) metal sensors. Bi electrodes offer a well defined, undistorted and highly reproducible stripping response, excellent resolution of neighbouring peaks, high hydrogen evolution, wide linear dynamic range, with signal to background characteristics comparable to those of common Hg electrodes. While amalgam formation is responsible for the stripping performance of Hg electrodes, the attractive and unique behavior of Bi film electrodes can be attributed to the formation of multi-component alloys. Bi is known to form binary or multi-component (low-temperature melting) fusible alloys with numerous heavy metals, including lead (Pb), cadmium (Cd), thallium (Th), antimony (Sb), indium (Ir), or gallium (Ga)[10]. Such formation of low-temperature alloys facilitates the nucleation process during the deposition of heavy metals. As will be illustrated in the following sections, such emergence of effective non-mercury electrodes has a profound impact upon the electroanalysis of trace metals. This review article summarizes the recent development, attractive behavior, and applications of bismuth electrodes for electrochemical stripping analysis.

## HISTORICAL BACKGROUND OF BISMUTH FILM ELECTRODE

Bismuth electrodes were introduced in 2000 by Joseph Wang and his group in the New Mexico State University, USA. They fabricated Bi film on glassy carbon (GC) and carbon fiber substrates for ASV measurements of heavy metals such as Hg, Pb and Cd[11]. Later, his group as well as the group of Ogorevc in Slovenia demonstrated that Bi coated GC electrodes offer an extremely attractive stripping voltammetric performance, that compares favorably with that of Hg electrodes[12-17]. Parallel investigations in the Czech Republic focused on stripping voltammetry and potentiometry at bismuth-coated carbon paste electrodes[18, 19]. Subsequent work by Bobrowski[20, 21] and Economou[22, 23] extended the scope of bismuth electrodes to adsorptive stripping measurements of trace metals that cannot be plated electrolytically.

## DESIGN OF BI-FILM STRIPPING ELECTRODES

The design of Bi electrode plays a major role in the performance of resulting stripping analysis. In most cases, a carbon substrate is used to support the Bi film. A variety of carbon electrodes, of different sizes and geometries, can be used. Such films can be prepared ex situ (preplated) or in situ (by adding 0.25-1.0 ppm bismuth(III) directly to the sample solution, and simultaneously depositing the target heavy metals and bismuth):

$$Bi^{+3} + 3e^- \rightarrow Bi^0 \quad (1)$$

$$M^{+n} + ne^- \rightarrow M(Bi) \quad (2)$$

The ASV response on a glassy-carbon substrate increases with the concentration of the bismuth ion at first and levels off above 200 ppb[11]. Most commonly, an acetate buffer (pH 4.5) solution, containing the bismuth ions, is used as the plating solution. Such electrodes can perform reproducible multiple stripping runs in connection to an electrochemical cleaning (involving holding them at -0.25 V (vs. Ag/AgCl) for 30 s after each stripping step.

Disposable metal sensors can be fabricated by combining Bi coatings with low cost electrodes transducers. Wang et al. had shown that Bi coated screen printed electrodes offer reliable ASV measurements of trace Pb[15]. The attractive behavior of the new disposable “mercury-free” carbon strip electrodes, coupled with the negligible toxicity of bismuth, hold great promise for “one-shot” decentralized metal testing. Another promising route for preparing low-cost (disposable) bismuth-based metal sensors involves the use of graphite pencil electrodes[23]. Bismuth films can thus been prepared in situ on the pencil-based graphite substrate by depositing simultaneously the metal-analyte (Pb, Cd and Zn) and bismuth ions at -1.40 V. The corresponding detection limits are 0.3 ppb Cd and 0.4 ppb Pb and Zn.

In addition to bismuth film electrodes, it is possible to use bulk bismuth disk electrodes[24]. The stripping performance of such polycrystalline bismuth electrode is comparable to that of bismuth or mercury film electrodes. The bulk bismuth electrode, however, displays a slightly lower hydrogen overvoltage compared to Bi film electrodes.

## STRIPPING MODES

Different types of stripping analysis have been successfully employed in connection to bismuth electrodes. While most early studies have been devoted to ASV measurements, recent activity expanded the scope of bismuth electrodes to adsorptive and potentiometric stripping experiments. TABLE 1 illustrates the representative stripping applications of Bi film electrodes.

**TABLE 1 : Stripping applications of Bi electrodes.**

| Element | Matrix | Stripping mode | Type of Bi electrode |
|---|---|---|---|
| Cd, Co | Soil | ASV, AdSV | Film |
| Cr | River water | AdSV | Preplated film |
| Pb | Blood | ASV | Film on diamond |
| Zn | Pancreatic islets | ASV | Preplated film |

## POTENTIOMETRIC STRIPPING ANALYSIS

Hoeevar et al.[14] combined bismuth-film electrodes with a potentiometric stripping experiments. The constant-current potentiometric stripping approach was shown to compare favorably with analogous voltammetric stripping protocols, offering attractive signal-to-background characteristics and peak resolution. Well-defined sharp stripping peaks were observed for Cd, Pb and Zn, along with an extremely low baseline and hence sub-ppb detection limits.

## ADSORPTIVE STRIPPING VOLTAMMETRY AT BISMUTH FILM ELECTRODES

Adsorptive stripping voltammetry (AdSV) involves the formation and adsorptive accumulation of surface-active complexes of the target metal. This technique has greatly enhanced the scope of trace-metal measurements at bismuth electrodes. Wang and Lu[17] demonstrated the first adsorptive stripping operation of bismuth-film electrodes. The preplated bismuth electrode (on a glassy-carbon substrate) was shown to be extremely useful for adsorptive stripping measurements of trace nickel using dimethylglyoxime (DMG) as a complexing agent. Krolicka et al.[20] reported on the use of DMG for catalytic-adsorptive stripping voltammetry of trace cobalt at preplated bismuth film electrodes. Addition of $NaNO_2$ provided a 15-fold signal enhancement due to the catalytic effect occurring during the reduction of the adsorbed Co(II)-DMG complex. An extremely low detection of 70 ppt was obtained with a 1 min accumulation, along with high sensitivity and reproducibility.

## SUMMARY

Bismuth electrodes have already found a wide range of environmental and clinical applications. Hutton et al.[25] used a bismuth film for stripping measurements of cobalt and cadmium in soil extract samples. Kadara and Tothill[26] used stripping potentiometry at a bismuth-coated screen-printed carbon electrode for measuring lead and cadmium in soil extracts and waste water obtained from polluted sites. Compton's group reported on the detection of lead in human blood using a bismuth-film modified boron-doped diamond electrode in connection to an acoustically-assisted deposition procedure[27]. These are some examples of real life applications of Bi film electrodes.

This review article has summarized recent development in bismuth electrodes for stripping-based electrochemical measurements of trace metals. The development of reliable non-mercury electrodes is considered a major challenge for electroanalysis. Bismuth electrodes offer an attractive alternative to mercury electrodes, with attractive signal to background characteristics and peak resolution. Further studies are required for obtaining a better understanding of the preparation-structure-performance relationship of different types of bismuth electrodes and for assessing their overall scope and power.

## ACKNOWLEDGEMENT

We acknowledge financial support from the project funded by the UGC, New Delhi (grant no. PSW-038/10-11-ERO).

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