Bismuth is replacing mercury in modern sensor science

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Abstract: Bismuth electrode is presented and characterized as an attractive non-toxic replacement for the commonly used mercury electrode in advanced electrochemical detection of trace heavy metals and some selected organic compounds. Bismuth electrodes were prepared as conventional size electrodes and as micro-electrodes, the latter imparting great possibilities for application in micro-volumes and at micro-locations. In particular, for trace heavy metal detection, bismuth electrodes compare favorably with those of mercury or in certain cases even surpass them. In connection with stripping voltammetry and stripping potentiometry, bismuth electrodes allow multi-element detection down to low μg/L levels of heavy metals.

Keywords: bismuth electrode, trace heavy metals, electroanalysis

INTRODUCTION

Mercury has attracted immense attention since it was recognized as an element with many adverse effects upon the biosystem. One of the fields where mercury has been commonly present is certainly that of the electroanalysis of trace heavy metals and some organic compounds. Its first application as an electrode in polarography was reported in 1922 by Prof. Jaroslav Heyrovsky, who was later awarded a Nobel prize. Since then, because of several electrochemical advantages such as high overpotential for hydrogen reduction, mercury electrodes have found widespread application, in particular for trace heavy metal detection in connection with stripping voltammetry and stripping potentiometry. Both techniques are based on mercury's inherent ability to electrochemically preconcentrate heavy metals, usually as amalgams, intermetallic compounds or as adsorbed metal complexes, thus allowing measurements down to μg/L concentration levels. However, due to the well known toxicity of mercury and inconvenience in its handling, the popularity of mercury electrodes has considerably declined in the past, particularly in the last decade. There have been many attempts to replace mercury with other electrode materials and coatings, such as gold, platinum, iridium, different carbon modifications, etc., but the overall performance has not approached that of mercury. Thus, there remains a growing interest in finding new electrode materials and coatings to replace mercury.

Very recently, the "environmentally friendly" bismuth electrode[1] was presented as an attractive alternative for the detection of some trace heavy metals and selected organic compounds. It possesses better mechanical stability together with an electroanalytical performance that compares favorably with its mercury counterparts[2-7]. Preliminary stud-

ies have revealed that the non-toxic bismuth electrode holds great promise, particularly in meeting growing demands for environmental and industrial monitoring, decentralized clinical testing and remote sensing, where the presence of mercury is undesirable or even restricted.

RESULTS AND DISCUSSION

With the aim of assessing the electrochemical performance of the bismuth electrode, a critical comparison with the mercury electrode was performed. Figure 1 displays stripping voltammetric signals for 50 μg/L of zinc, cadmium and lead obtained at mercury (a) and at bismuth (b) micro-electrodes. The stripping voltammograms exhibit undistorted and well-defined signals for all three heavy metals, together with excellent resolution. The peak potentials for zinc and lead are nearly the same, whereas the signal for cadmium appears at a more negative potential (at -0.79 V) in the case of the bismuth electrode. This characteristic presents the possibility for simultaneous detection of thallium in the presence of cadmium and lead, which is a common problem at the mercury electrode due to signal overlapping (not shown). In addition, it is evident that the bismuth electrode does not compromise the signal to background ratio in the presence of dissolved oxygen.

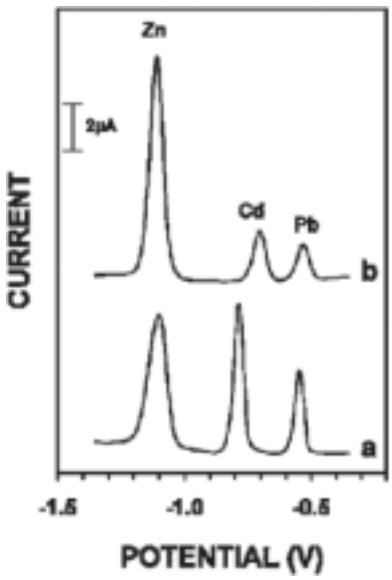

Figure 1. Stripping voltammograms for 50 mg/L of zinc(II), cadmium(II) and lead(II) at mercury (a) and bismuth (b) micro-electrode in 0.1 M acetate buffer solution (pH, 4.5) in the presence of dissolved oxygen. Deposition for 120 s at -1.4 V. Square-wave voltammetric stripping scan with a frequency of 20 Hz, potential step of 5 mV, and amplitude of 25 mV.

The use of bismuth electrode revealed an excellent reproducibility for all three metals investigated with a calculated limit of detection of, e.g., 0.3 μg/L for lead, in combination with a 10 minute preconcentration period. Similarly, several other heavy metals can be measured, such as indium, thallium, copper, cobalt, and nickel. Research efforts to expand the scope of applications of the bismuth electrode for the detection of some other heavy metals are in progress.

CONCLUSIONS

Bismuth electrode imparts great possibility for tailoring different kinds of electrochemical sensors for trace heavy metals and some organic compounds. It enables the introduction of electrochemical detection to those areas, where the use of mercury electrodes is not convenient or not possible, e.g., *in vivo* measurements, flow analytical techniques, on-field environmental measurements, etc. In addition, bismuth electrode obviates the need for special handling, which is required

for mercury and addresses the problems connected to mercury disposal. Therefore, the successful replacement of mercury with nontoxic bismuth raises expectations for a renaissance in stripping electrochemical detection in modern analytical chemistry.

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