

# Bismuth-Film Electrode for Voltammetric Analysis

Valéria Guzsvány<sup>#</sup>

Department of Chemistry, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, R. Serbia

Nowadays in numerous electroanalytical laboratories many types of bismuth-film electrodes (BiFEs) have been proven to be applicable for different target analytes, first of all the heavy metal traces, mostly in batch working regime [1,2]. Recently, Wang et al. [3], Vytřas et al. [4], Hutton et al. [5], Królicka and Bobrowski [6], Charalambous and Economou [7] and Legeai and Vittori [8] applied BiFEs electrodeposited onto different substrate electrode from plating solutions containing different concentration of bismuth (III) ions without or with complexing agents for use in trace level analysis of target metals, usually by anodic stripping voltammetry (ASV, e.g. Cd, Pb, Zn, In, etc.) or adsorptive stripping voltammetry (AdSV, e.g. Ni, Co). The advantageous analytical properties of BiFEs, roughly comparable to those of MFEs, are attributed to the property of bismuth to form "fused alloys" with heavy metals, which may be analogous to the amalgams that mercury forms with a similar sensitivity [1,2,8] (usually ppb or lower). Very recently, different BiFEs were applied for direct determination of some organic compounds (pesticides and organic dyes) at ppm level [9-12]. In contrast to the MFE, BiFEs are insensitive to the dissolved oxygen, which is a significant advantage for on-site monitoring of trace pollutants. However, some BiFE types have limitation, especially in on-site analysis [8], because at higher pH values bismuth-hydroxide formation can change the sensor surface.

The literature reports about ASV [13, 14] or amperometry [9] coupled with flow-injection analysis (FIA) in on-line systems described the improvement of analytical performance of methods based on different bismuth-film detector electrodes and the possibility of automation.

Recently, Kefala and Economou elaborated the on-line sequential-injection analysis (SIA)/ASV method for preparation of BiFE on glassy carbon (GC) substrate electrode, previously modified with a Nafion-film, and determination of selected metals at trace levels [13]. In this concept (Fig. 1) the polymeric coated GC forming part of the flow-through electrochemical cell, and the BiFE generation, analyte preconcentration, voltammetric measurement and electrode cleaning steps were combined on-line. The carrier buffer, bismuth(III) plating solution and samples were moved by a peristaltic pump, and a 10-port multi port selection valve served as the selection/injection valve. The control of the SIA and voltammetric equipments was accomplished by the same software application, which enabled the complete automation of the process. The measurement frequency was between 10 and 20 h<sup>-1</sup>, depending on the sample volume aspirated.

As a continuation of this work Economou and Voulgaropoulos introduced the hybrid flow-injection/sequential-injection "flow system" coupled with on-line ASV for trace level determination of Cd(II) and Pb(II) by ASV and Ni(II) and Co(II) by AdSV at a flow-through BiFE [14]. In this concept the authors combined the unidirectional flow of solution, the peristaltic pump for solution transport and the introduction of the solution by injection of discrete zones from FIA methodology with the single channel manifold, the multi-port selection valve as the sample introduction devices and the time-based sequential

introduction of solutions from SIA methodology.

Further, very recently other environment-friendly, very promising thin-film electrodes, the antimony [15] and gallium film [16] electrodes were introduced for electrochemical stripping analysis.

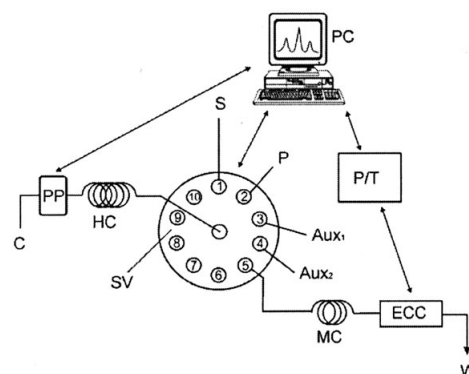


Fig. 1. Schematic diagram of the SIA/ASV manifold. PP, peristaltic pump; C, carrier; HC, holding coil; MC, mixing coil; PC, personal computer; P/T potentiostat; ECC, electrochemical cell; SV, selection valve; W, waste; S, sample; P, bismuth plating solution; Aux<sub>1</sub>, Aux<sub>2</sub>, auxiliary lines for calibration or standard addition purposes [13].

Having in mind the place of bismuth and antimony in the periodic system of elements, and the above experience these electrodes are probably related thin-film electrodes.

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<sup>#</sup>Current address: Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 774 Motooka, Nishi-ku, Fukuoka 819-0395, Japan