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# Employing a magnetic field to amplify zinc signal obtained at bismuth film screen-printed electrodes generated using dual bismuth precursor

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ABSTRACT

Two precursors of bismuth film – $Bi_2O_3$ and Bi(III) ions – and a favorable orientation of the magnetic field were exploited to increase the Zn signals recorded at screen-printed electrodes modified with a bismuth layer. When using this configuration and an in-situ procedure, Zn(II) signals were better shaped and much more sensitive than those obtained for conventional bismuth-modified screen-printed electrodes. The developed procedure exhibits linear behavior from 4 to 199 $\mu g\,l^{-1}$ Zn(II) with satisfying reproducibility (5%) and an low LOD of 0.05 $\mu g\,l^{-1}$. The method was applied for the determination of Zn(II) in fly ash extracts and mineral waters.

## 1. Introduction

Zinc is a common element in the environment and plays an important function in many biological processes of all living organisms. The biological role of zinc was thoroughly discussed in paper [1]. Its concentration in the environment may be affected by its use in products and its presence in raw materials. This is also true of building materials produced using alternative raw materials such as fly ash [2], a by-product of burning finely ground coal in a boiler during energy generation. Building material constituents, including zinc, can leach into the environment and contaminate it [3]. Water extracts from building materials are rich in sulfate and calcium ions, which cause problems when spectrometric methods (ICP-MS, ICP-OES) are used for the determination of metals [4].

Electrochemical techniques are as sensitive as spectrometric methods and may be used for the detection of toxic metal ions in various samples. The high ionic strength of examined solutions is not a problem in the case of electroanalysis, but may even be considered an advantage. Furthermore, unlike spectrometric methods, electrochemical techniques are suitable for miniaturization and on-site applications. Using microfabrication techniques (e.g. chemical or physical vapor deposition coupled with photolithography) or screen-printing techniques [5,6], it is possible to produce planar electrodes for electrochemical sensors; one example of such electrodes includes the widely applied glucose test strips. The applicability of anodic stripping voltammetry (ASV) coupled with screen-printed (SPEs) and/or microfabricated electrodes for the determination of metals concentrations in numerous samples has been demonstrated using both mercury-based and mercury-free electrodes [5–9] with particular reference to bismuth film electrodes [9–14].

At the same time, it has been reported that it is difficult to determine zinc content using bismuth-modified electrodes, since its signals are hindered by the high background current originating from the reduction of hydrogen ions. For the above reason, the limits of Zn detection have usually been much higher [5–9] than those obtained for Pb or Cd at the same bismuth film electrodes. There are few works reporting the voltammetric determination of Zn using SPEs [15–28] or microfabricated electrodes [29–31], and only some of them discuss the analysis of real samples (tap water [20], lake water [21], seawater [22], smelter sewage after treatment [23], waste water certified reference material [24], spiked river water certified material [25], herb samples [26], extracts from sediments [27], human sweat [28] and serum [29–31]). The authors employed modified SPEs prepared using commercial carbon inks or commercially available sensors as supports. In the majority of applications, bismuth was used as the modifier of carbon SPEs. The bismuth electroactive layer was generated via the electrolysis of a bismuth-containing solution (both ex-situ and in-situ) or via the electroreduction of the bismuth precursor ($Bi_2O_3$, $BiPO_4$) dispersed and immobilized at the surface of the SPE. Alternatively, the chemically synthesized

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bismuth nanoparticles were immobilized on the SPE surface using Nafion.

The aim of this project was to elaborate a novel, very sensitive anodic stripping voltammetric procedure of Zn detection at an in-situ plated bismuth-modified screen-printed electrodes and to apply them for the determination of Zn(II) in calcium- and sulfate-rich samples (fly ash extracts and mineral waters). To meet this objective and to amplify the Zn response, two processes were employed: an unprecedented modification of the SPE surface with a bismuth layer originating from two precursors ($Bi_2O_3$ and Bi(III) ions) and a favorable orientation of the magnetic field with regard to the working electrode during bismuth film deposition. The data obtained for water extracts of fly ash were used to assess the release of Zn(II) from fly ash used as a component of building materials into the environment.

## 2. Experimental

### 2.1. Apparatus and instrumentation

Electrochemical measurements were performed using an Autolab PGSTAT204 (Nova 1.10.1.9 software) potentiostat with a standard three-electrode configuration. The screen-printed electrodes (4 mm in diameter; carbon DRP 110 and bismuth-oxide-modified DRP 110BI) were provided by Dropsens, Spain. The magnetic stirrer (Metrohm 801) was controlled with the NOVA software. The magnet built into the stirring device induced a magnetic field of up to 86 mT, while the field induced by the 7 mm long stirring flea was up to 3 mT.

Photolysis was performed using a UV digestion system with a 150 W lamp (Mineral, Poland).

The morphology of the deposits was evaluated using a Nova NanoSEM 200 (FEI, USA) scanning electron microscope (SEM) with an elemental energy dispersive X-Ray microanalyser.

### 2.2. Reagents

All solutions were prepared using deionized water with a resistivity of 18.2 MΩ (Millipore, Simplicity UV). The following reagents (analytical grade, POCH, Poland) were used without further purification: 30% $H_2O_2$, $CH_3COOH$, $CH_3COONH_4$, $Bi(NO_3)_3{\cdot}5H_2O$. A 1 M $CH_3COONH_4$ (pH = 6.9) was used as the supporting electrolyte. Standard solution containing Zn(II) at a concentration of 1.0000 g $l^{-1}$ was obtained from Merck and diluted as required.

### 2.3. Procedures

#### 2.3.1. Extraction Procedure

The extraction procedure was performed according to the EN 12457-2:2002 standard. 90 g of ash were placed in a polypropylene bottle and mixed with 900 ml of distilled water (room temperature). The bottle was then sealed and placed in a rotary agitator (extractor) (36 rpm, bottles placed at an angle of 45 degrees to the axis of rotation) for 24 h. After mixing, the samples were filtered, and the pH and conductivity were measured. The fraction of the extract used for voltammetric determination was acidified to pH 2 using concentrated HCl Suprapur (Merck).

#### 2.3.2. Measurement procedure

In all experiments, the in-situ procedure was used for film deposition. Prior to the experiments, the SPE electrode was immersed in the tested solution for 1 minute. The accumulation potential of −1.5 V was then applied for 300 s and the DPV voltammogram was recorded within the range of −1.5 V to 0.3 V. During accumulation, the solution was stirred using a magnetic bar. The parameters of the DPV mode were as follows: $E_{ini} = -1.5$ V, $E_{end} = 0.3$ V, $\Delta E = 25$ mV, $E_s = 5$ mV, $t_{eq} = 5$ s. Peak area was used to evaluate the analytical signal [32].

#### 2.3.3. Sample characteristics

The tested fly ash samples originated from thermal power stations in Poland. Two batches of fly ashes were sampled from the electrostatic precipitator of two different fluidized bed lignite-fired boilers; they are referred to as sample FL1 and FL2. The third sample, labeled FL3, came from an electrostatic precipitator attached to a bituminous coal-fired boiler.

The water samples in polyethylene terephthalate (PET) bottles were purchased from a local store: still mineral water, labeled MW1, and carbonated mineral water, labeled MW2.

## 3. Results and discussion

### 3.1. Voltammetric cell configuration and evaluation of the performance of different modified screen-printed electrodes plated with bismuth

To develop an ASV procedure of Zn(II) quantification at the BiF-SPCE with high sensitivity and a low LOD, three objectives needed to be achieved:

1) Improved transport of electroactive substances – Bi(III) that forms the films and low-temperature melting alloys with the determined metals – to the surface of the electrode, and increased nucleation of bismuth and the co-deposited metals in a field generated by the magnet built into the magnetic stirrer.
2) In-situ modification of the surface of the graphite screen-printed electrode with a bismuth layer generated as a result of the simultaneous reduction of the two precursors: bismuth oxide dispersed into the electrode material and Bi(III) ions added to the investigated solution.
3) The utilization of the deposited bismuth film's diamagnetic properties, which allow the forces acting in the magnetic field to prevent bismuth crystallites from leaving the surface of the electrode, and at the same time affects its orientation relative to the magnetic field and, consequently, the surface of the electrode.

#### 3.1.1. Configuration of the voltammetric cell and magnetic stirrer

To reduce the amount of chemicals used up during the experiments, the classic 10 milliliter voltammetric cell was replaced with a 10 mm disposable spectrophotometer polystyrene square cuvette. The volume of the solution necessary to conduct the voltammetric experiment was thus reduced from 10 to 3.2 ml. The use of square cuvettes allowed the magnetic stirrer to be used in an unconventional manner.

The magnetic stirrer was laid on its side (Fig. 1A, B) and the clear smooth side of the cuvette was pressed against the center of the stirrer's base. As a result of this arrangement, the stir bar's plane of rotation was parallel to the working electrode's surface. Shifting the cuvette together with the electrode immersed in it in relation to the center of the magnet built into the magnetic stirrer made it possible to change the position of the electrodes in relation to the lines of the magnetic field generated by the magnet.

#### 3.1.2. Evaluation of the performance of different screen-printed electrodes

In the case of bismuth-free SPEs, Zn(II) signals were not observed. The application of the $Bi_2O_3$—modified carbon SPEs ($SPE_{ox}$) or a simple graphite SPE plated in situ with bismuth ($SPE_{insitu}$) resulted in the appearance of well-shaped Zn(II) signals.