



# A miniaturized electrode system for voltammetric determination of electrochemically reducible environmental pollutants



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## ABSTRACT

A newly designed miniaturized electrode system (MES) based on a mercury meniscus modified silver solid amalgam electrode as the working electrode was developed for voltammetric determination of electrochemically reducible organic compounds in small sample volumes. Genotoxic 2-aminofluoren-9-one (2-AFN) was chosen as a model environmental pollutant in this study to test the performance of the introduced MES. The determination of 2-AFN was carried out by differential pulse voltammetry in 100  $\mu\text{L}$  samples under following conditions, using two different ways of air oxygen removal: (i) a supporting electrolyte methanol–Britton–Robinson (BR) buffer of pH 4.0 (1:9, v/v), with regeneration potentials  $E_{\text{reg},1} = 0 \text{ mV}$  and  $E_{\text{reg},2} = -1200 \text{ mV}$  and with oxygen removal by bubbling with nitrogen, and (ii) a supporting electrolyte methanol–BR buffer of pH 10.0 (1:9, v/v), with regeneration potentials  $E_{\text{reg},1} = -200 \text{ mV}$  and  $E_{\text{reg},2} = -1600 \text{ mV}$  and with oxygen removal by the addition of solid sodium sulfite as a reducing agent. The calibration curves were measured in the concentration range from 1 to 100  $\mu\text{mol L}^{-1}$  of 2-AFN, with the limits of quantification about 1  $\mu\text{mol L}^{-1}$  reached in both media. The practical applicability of the newly developed voltammetric methods using the MES was successfully verified on the direct determination of 2-AFN in model samples of drinking and river water.

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## 1. Introduction

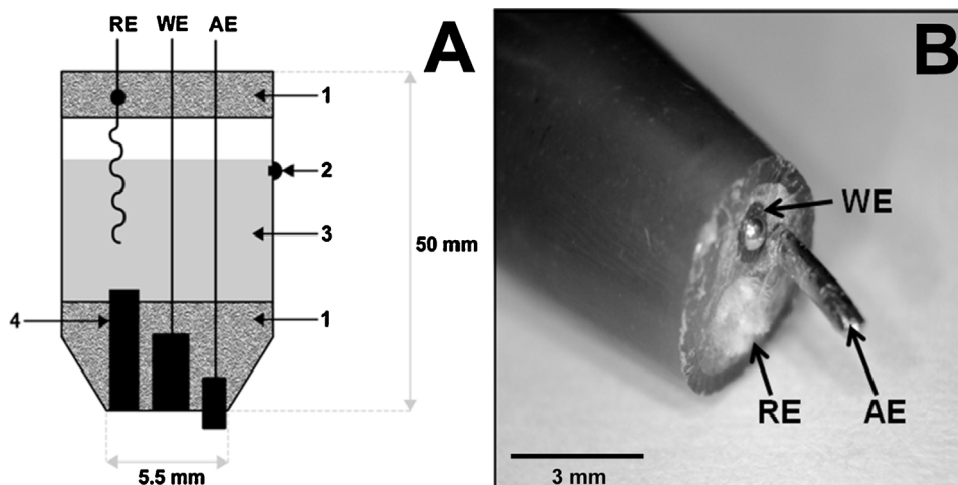
Analytics and monitoring of environmental pollutants belong among the most dynamically developing branches of chemical analysis nowadays [1–3]. Electrochemical techniques have merits of simplicity, rapidity, high sensitivity, specificity, reduced power requirements, ease of microfabrication, good compatibility with biological samples, and low investment and running costs [4,5]. These characteristics make electrochemistry uniquely suitable for integration in miniaturized devices [5]. The miniaturized analytical devices and their applications are a highly hot topic in modern analytical chemistry in the latest several years [5,6]. The miniaturized systems have been applied in a variety of areas including biochemical assays, immunoassays, biosensors as well as clinical diagnostics, environmental monitoring, biochemistry, proteomics, and cell biology [5]. They have many advantages such as portability, possibility of analysis of small sample volumes (e.g., miniaturized electroanalytical devices allow the use

of microliters of a sample solution instead of milliliters as in the case of conventional electrochemical cells [7,8]), and possibility of field measurements. A portability of the miniaturized system can be used especially for applications outside the laboratory environment in order to overcome drawbacks of conventional analytical procedures, which commonly involve the collection of a sample at one location and then a delay while the sample is sent to the laboratory, processed and analyzed in the laboratory [5,9,10].

The presented work is focused on the introduction and application of a miniaturized electrode system (MES) utilizing a mercury meniscus modified silver solid amalgam electrode (m-AgSAE) as the working electrode, which was constructed for voltammetric determination of electrochemically reducible organic compounds in small sample volumes. Since cathodic electrochemical detection suffers from interference by dissolved air oxygen, two ways of its removal were tested: (i) by bubbling with nitrogen and (ii) by adding solid sodium sulfite as a reducing agent. Genotoxic 2-aminofluoren-9-one (2-AFN) was chosen as a model environmental pollutant, and a sensitive differential pulse voltammetric (DPV) method for its determination was developed using the MES and applied in simple environmental matrices – drinking and river waters.

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**Fig. 1.** Scheme (A) and photography (B) of the miniaturized electrode system (MES). RE – reference silver–silver chloride electrode; WE – working silver solid amalgam electrode; AE – auxiliary platinum electrode; 1 – epoxy resin; 2 – hole and plug; 3 – saturated KCl solution; 4 – porous matter (filter paper, cotton, etc.).

### 1.1. Miniaturized electrode system

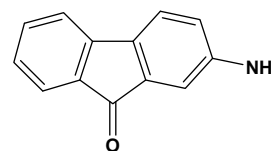
The newly designed MES for voltammetric determination of electrochemically reducible organic compounds in small sample volumes is introduced and described for the first time in this paper. The main benefits of this prototype are: the possibility of simple field measurements without the need to carry fragile electrodes (e.g., the glass ones), its easy portability when it is connected to a small-size electrochemical analyzer and a notebook or tablet, and the possibility of high-throughput and automatic measurements in microliter sample volumes (using a microtiter plate as a system of electrochemical cells).

The scheme of the MES is shown in Fig. 1. The body of the MES was made from the 1 mL micropipette tip. The MES contains three electrodes: (i) the working electrode (WE) (a silver solid amalgam electrode which can be either polished or covered by mercury film or mercury meniscus), (ii) the reference saturated silver–silver chloride electrode (RE) (Ag|AgCl|saturated KCl), and (iii) the auxiliary electrode (AE) (2 mm long platinum wire of 0.8 mm diameter). The porous matter (4) (filter paper, cotton, etc.) ensures electrolytic contact between the inner solution (3) (saturated KCl) and the measured solution. The bottom and upper parts of the body set were sealed by epoxy resin (1). The hole in the upper part of the body set (2) served for filling the inner reservoir by the saturated KCl solution. This hole is closed by a plug.

The MES is designed to be a stable and mechanically resistant sensor for long-term use. If there are any changes in its electrochemical performance in time (e.g., increasing background current/noise or changing shape/position of the analyte peak), simple regeneration procedures can be performed either with the working or reference electrode, respectively: (i) amalgamation, electrochemical activation, or electrochemical regeneration of the working electrode (see Section 2.3) or (ii) refill of the inner solution (saturated KCl) of the reference electrode.

### 1.2. Model environmental pollutant

In this work, 2-AFN (see Fig. 2) was selected as a model compound for testing the MES with the m-AgSAE. (See our previous papers [11–13] describing various types of amalgam electrodes). 2-AFN belongs to derivatives of polycyclic aromatic hydrocarbons derived from better-known fluoren-9-one [14]. 2-AFN is known as a hazardous substance with genotoxic effects [15], whose occurrence in the environment is associated mainly with the processing



**Fig. 2.** Structural formula of 2-aminofluoren-9-one (2-AFN).

and purification of natural gas in gas refineries [16,17]. In the past, the genotoxic effect of 2-AFN was investigated, and the formation of a DNA–2-AFN complex was confirmed [15,18]. The negative effect of 2-AFN was also observed in our recent study in which an electrochemical DNA biosensor was used for investigation of the interaction between 2-AFN and double-stranded DNA [19].

Taking into account that 2-AFN contains two electrochemically active functional groups – cathodically reducible oxo group and anodically oxidizable amino group – bonded to the aromatic rings of fluorene, modern polarographic and voltammetric techniques can be utilized for its sensitive determination. Recently, polarographic and voltammetric methods for the determination of 2-AFN at a classical dropping mercury electrode [20], at a hanging mercury drop minielectrode (HMDmE) [20,21], at a m-AgSAE [22], and at a glassy carbon electrode [19] were developed. Their practical applicability was verified on the direct determination of 2-AFN in model samples of drinking and river water [19–22], and their analytical performance was also compared with two spectrometric methods (UV spectrophotometry and fluorimetry) [22], when significantly lower limits of quantification were obtained using electrochemical methods.

## 2. Experimental

### 2.1. Chemicals

A stock solution of 2-AFN (98%, Sigma–Aldrich, Saint Louis, MO, USA) ( $c = 1 \times 10^{-3} \text{ mol L}^{-1}$ ) was prepared in methanol (for HPLC,  $\geq 99.8\%$ , LiChrosolv, Merck, Darmstadt, Germany). A UV–vis spectrophotometric study demonstrated that the methanolic stock solution is stable for at least 3 months [20]. More diluted solutions were prepared by dilution of the stock solution with methanol. Britton–Robinson (BR) buffers were prepared in a usual way [23]; boric acid, phosphoric acid (85%), acetic acid (99%), and sodium hydroxide (all of p.a. purity) were supplied by Lach-Ner, Neratovice, Czech Republic. A  $0.2 \text{ mol L}^{-1}$  acetate buffer of pH 4.0 (a solution of

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