



Cadmium determination in natural water samples with an automatic multisyringe flow injection system coupled to a flow-through screen printed electrode

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ABSTRACT

Heavy metals, as cadmium, attract a rising attention in environmental studies due to their increasing release by human activities and acute toxicity. In situ analytical methods are needed to minimize current uncertainties caused by the transport and conservation of samples. Here, we present the completely automatic determination of Cd in natural waters using a newly developed screen printed electrode sensor (SPE), inserted in a homemade purpose-built flow cell coupled to a Multi-Syringe Flow Injection Analysis system (MSFIA). The working electrode of SPEs was constituted by a carbon film modified with Nafion. Cd was plated on an in situ bismuth film and determined using Square Wave Anodic Stripping Voltammetry. Different chemical conditions of deposition and stripping were studied. A sample/acetic buffer mixture was found to be a well suited medium to form the Bi film and perform the analysis. Cd was quantified via calibration by on line standard additions. The limit of detection was found to be $0.79 \mu\text{g L}^{-1}$, well below the limit stipulated by the European directive ($5 \mu\text{g L}^{-1}$). Good sample throughput (14 h^{-1}) and low consumption of reagent and sample (1.3 mL) were also obtained in line with previous works in Cd flow analysis.

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1. Introduction

Heavy metals represent a risk for ecosystems and humans due to their toxicity and bioaccumulation. Therefore, governments require a strict control of their concentrations in natural systems; cadmium concentrations in drinking waters must be lower than $5 \mu\text{g L}^{-1}$ according to European directives (RD 140/2003), EPA [1] and WHO. The control of the concentration of heavy metals requires reliable, rapid and portable analytical techniques that can quantify lower concentrations than those allowed by regulations.

Spectrometric techniques such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy or Mass Spectrometry (ICP-AES and ICP-MS) and Atomic Fluorescence Spectrometry (AFS), although provide good sensitivity and excellent selectivity [2,3] cannot be used for in-field measurements since they involve expensive and large equipment. These techniques are also time consuming, and usually require some preconcentration steps to reach environmental levels [4]. On the other hand, electrochemical techniques require small, low cost

instruments, which can be portable to the field for in situ analysis and offer very low detection limits without sample preconcentration [3].

Cd has been widely determined by Anodic Stripping Voltammetry (ASV), conventionally performed on a hanging mercury drop electrode (HMDE) or a mercury film electrode (MFE) [2,5,6]. These electrodes have been adapted to flow systems to use the advantages of on-line analysis: automation, reduction of the risk of sample contamination and cost-effective operation, monitoring, etc. [7,8]. However, the toxicity of mercury has motivated the research on new materials, less poisonous and with similar electrochemical performances to mercury [9].

In 2000, Wang introduced the bismuth film electrode (BiFE) as an alternative to the MFE [10]. Bismuth is environmentally better suited due to the lower toxicity of its salts. An excellent mechanical resistance makes the BiFE (a Bi alloy) more adequate than the MFE (a Hg amalgam) for coupling to flow systems [8,11]. At appropriated potentials the stripping of these electrodes leads to signals characterized by high sensitivity and reproducibility. Stripping voltammetry on BiFE is not affected by dissolved oxygen, but surfactants can produce undesired interferences [12]. Coating by polymeric membranes such as Nafion, has been proposed to modify the working electrode surface, to enhance the signal and to avoid surfactant effects [13,14].

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Bi can be plated on different materials such as glassy carbon, carbon paste, carbon fibre, carbon ink, carbon nanotubes, etc. [8,14]. In this work we have used carbon ink to manufacture a screen printed electrode sensor (SPE). The SPE has the three electrodes (working, counter and reference) concealed in a very small surface, permitting its attachment to a flow cell of small volume. This guarantees a complete renewal of the cell solution, reduces the dead volume and minimizes the consumption of both reagents and samples. Moreover, SPE has a low cost of production, and can be easily operated and replaced.

Initially, only mercury electrodes have been used in electrochemical flow systems of different configurations: continuous flow manifold [15], flow injection analysis (FIA) [16], sequential injection analysis (SIA) [7,17] and others. More recently, BiFEs have been coupled to different types of flow systems for the determination of Cd: sequential injection mono-segmented flow analysis (SI-MSFA) [18], hybrid flow-injection/sequential-injection (FIA/SIA) [9], a robotic system [19], batch injection manifold (BIA) [20] and others [8].

Multisyringe flow injection analysis (MSFIA) was presented by our group in 1999. The aim of MSFIA is to include, in the same methodology, the advantages of the previous FIA, SIA and MCFIA techniques. These are: high reproducibility and sample throughput, merging flow of multiple reagents, reduction of the consumption of reagents and the insertion of preliminary operations (preconcentration in solid supports, UV photo-oxidation and smart operations [21]). For that purpose an automated syringe pump is modified to attain the simultaneous movement of 4 syringes [22].

In this work, we have combined the use of a homemade carbon ink SPE inserted in a purpose-built flow cell with MSFIA in order to develop an automatic flow system to determine Cd concentrations

in natural samples. To the best of our knowledge, this is the first time such kind of MSFIA system is presented.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared in Milli Q ultrapure water (Millipore, Molsheim, France). Metal standards were prepared by dilution of Bi, Cd, Pb and Zn stock solutions (Scharlau, AAS standard, Barcelona, Spain). HCl solutions (0.01 mol L^{-1} , 1 mol L^{-1} and 4 mol L^{-1}) were prepared by dilution of HCl (Sigma Aldrich, ACS reagent, Germany). HCl 0.01 mol L^{-1} was employed as carrier. Acetate buffer was prepared by dissolving an appropriate amount of sodium acetate anhydrous (350 mmol L^{-1}) and sodium chloride (700 mmol L^{-1}), both from Sigma Aldrich (TraceSelect), and the pH adjusted to 4.6 by HCl 4 mol L^{-1} additions. Nafion stock solutions of 5% (w/v) in a mixture of low weight aliphatic alcohol and water (Aldrich Chemicals, Germany) were diluted until 0.5% (v/v) with water.

All plastic material and quartz tubes were cleaned by acidification in HNO_3 (10%) for at least 2 days, and thoroughly rinsed with Milli Q water immediately before use.

2.2. Apparatus

A complete scheme of the sensor is shown in Fig. 1A. Based in SPEs developed by the analysis of organic substances in different matrices [23,24], we developed new SPEs using carbon ink and a different size of working electrode. SPEs were produced with a 245 DEK (Weymouth, UK) screen printing machine. A detailed description of the printing procedure can be found elsewhere [23,24]. Graphite ink (Electrodag 421) from Acheson (Milan, Italy) was used

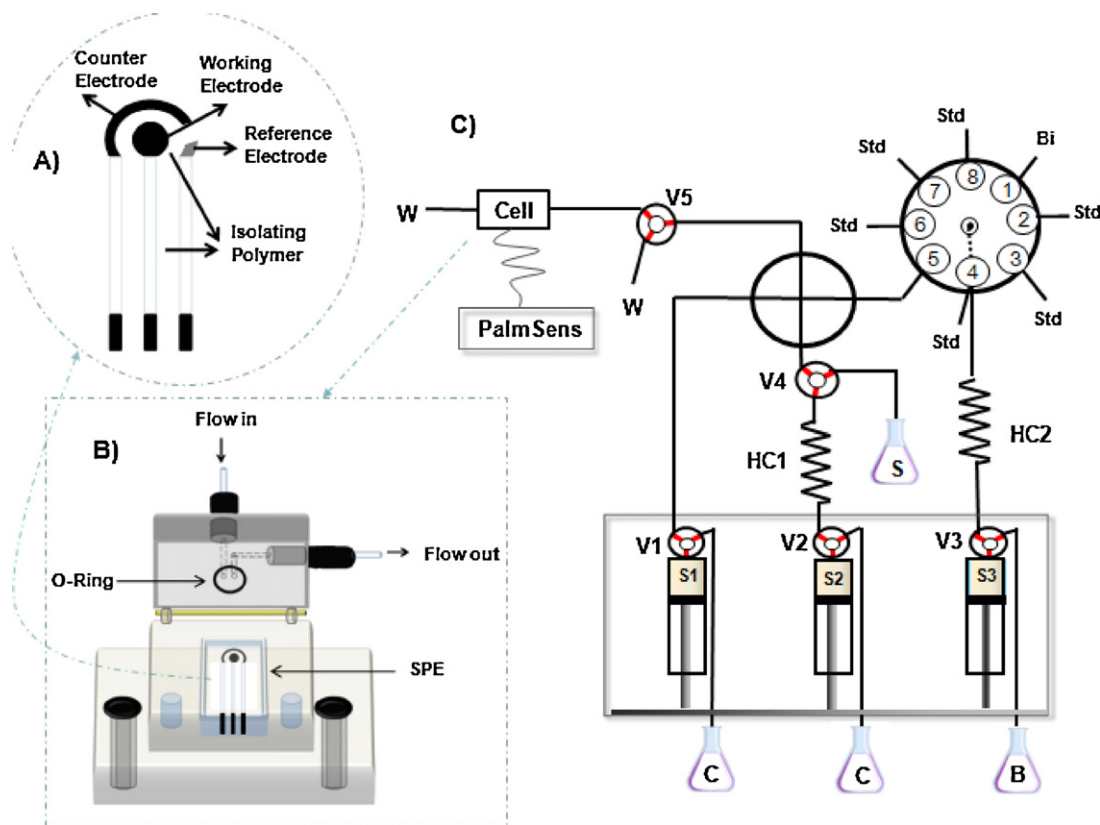


Fig. 1. Scheme of: (A) the screen printed electrode, (B) the flow cell and (C) the Multi Syringe-Flow Injection Analysis System manifold. V (V1–V5): valve; HC: holding coil; S (S1–S3) syringes, C: carrier, B: buffer, S: sample; Bi: $800 \mu\text{g L}^{-1}$ in $\text{HCl } 0.01 \text{ mol L}^{-1}$; Std: variable concentration of Cd and $800 \mu\text{g L}^{-1}$ of Bi in $\text{HCl } 0.01 \text{ mol L}^{-1}$; W: wasted; Cell: electrochemical flow cell.

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