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# 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 $\mu g L^{-1}$, well below the limit stipulated by the European directive (5 $\mu g L^{-1}$). 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.



## 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 $\mu g L^{-1}$ 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

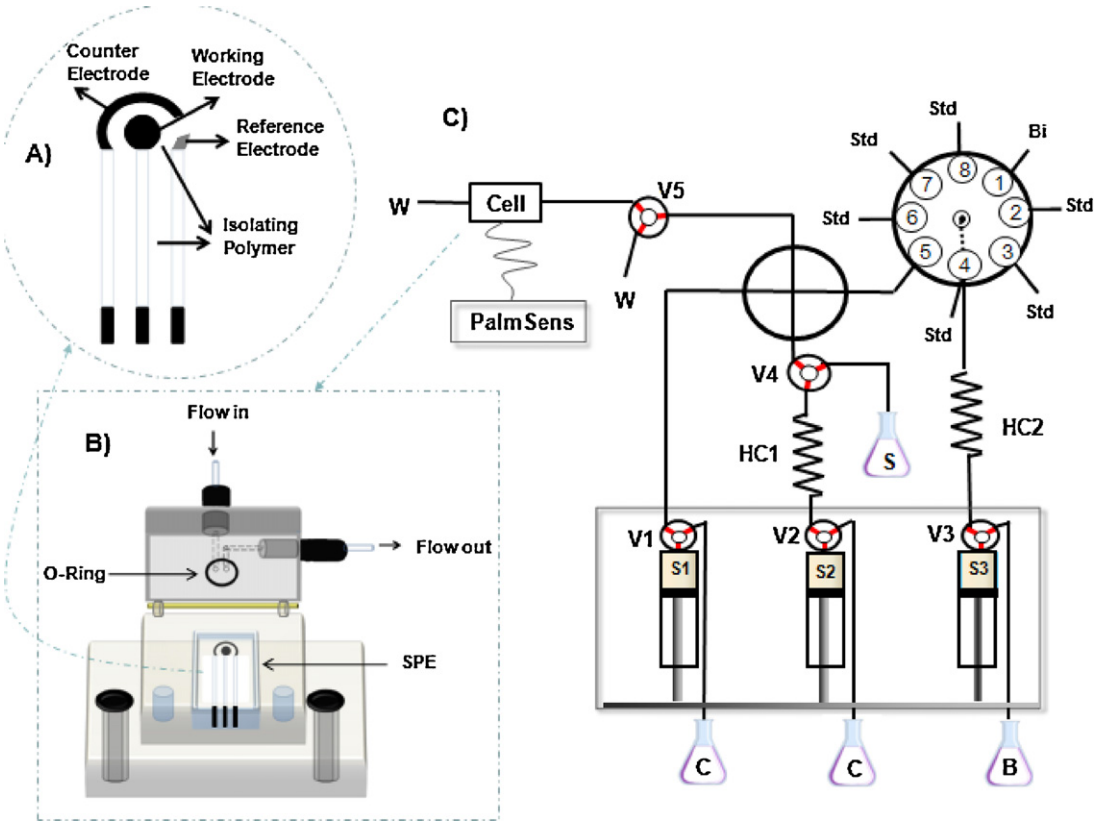


**Fig. 1.** Scheme of: (A) the screen printed electrode, (B) the flow cell and (C) the Multi Syringe-Flow Injection Analysis System manifold. V (V1–V5): valve; HC: holding coil; S (S1–S3) syringes, C: carrier, B: buffer, S: sample; Bi: Bi 800 μg $L^{-1}$ in HCl 0.01 mol $L^{-1}$; Std: variable concentration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

to print the working and counter electrode. Silver ink (Electrodag 477 SS) was used to print the pseudo-reference electrode. The substrate was a flexible polyester film (Autostat HT5) obtained from Autotype Italia (Milan, Italy). The electrodes were home produced in packs of 48 per polyester film. The diameter of the working electrode was 0.3 cm resulting in a geometric area of 0.07 $cm^2$.

The flow cell, was homemade and specially adapted for this particular SPE. This modified cell allows an easy and reproducible replacement of the SPE. An O-ring located at the cover helps to close tightly the electrochemical cell, confining the flow cell volume to 15 μL (Fig. 1B).

Into the MSFIA system (Fig. 1C), solutions flow by means of a multisyringe burette (BU4S; Crison Instruments, Barcelona, Spain) with programmable flow rates, which is able to handle up to four syringes as liquid drivers. In our manifold, the burette is equipped with just three glass syringes (Hamilton, Switzerland): two syringes of 1 mL (S1 and S3) containing the buffer (B) and carrier (C) solutions respectively and one of 5 mL (S2) also filled with carrier solution. All syringes are mounted on a common metallic bar and each one is provided with a three-way solenoid valve (V1–V3) (NResearch, West Caldwell, NJ); as a result, the three syringes are operated simultaneously. Depending on the position of each solenoid valve, the fluids contained in the syringe are loaded from the solution reservoirs (V1–V3: off) or dispensed to the flow network (V1–V3: on). An eight-port selection valve (SV) (Crison Allela, Barcelona, Spain) is connected to S3 via the holding coil HC2 and to the flow network via port 5. Port 1 is connected to a vessel containing 800 μg $L^{-1}$ Bi in HCl 0.01 mol $L^{-1}$ (Bi in Fig. 1C) to form the Bi film onto the SPE allowing the measurement of Cd in the sample. The rest of the free ports of SV (port 2–4 and 6–8) are connected to vessels containing the same Bi/HCl solution in the presence of increasing Cd concentrations (Std) in order to obtain the calibration curve. There are two additional solenoid commutation valves: V4 and V5 (MTV-3-N 1/4 UKG; Takasago, Japan). V4 is connected to S2 via HC1, to the sample vessel (S) and to V5 (V4 on: sample flows to HC1; V4 off: either the sample or carrier in HC1, flows to V5). V4 connections allow the load and change of the sample avoiding the contamination of the syringe. V5 is located just before the flow cell and permits the admission of the solution to the flow cell (V5: off) or to the waste (V5: on). A homemade 4-way connector of methacrylate (PMMA) is used as confluence point to mix sample, buffer and either the Bi or Bi/Cd solution. All network tubing is 0.8 mm internal diameter in poly(tetrafluoroethylene) (PTFE).

The execution of the analytical protocol is computerized by using the AutoAnalysis 5.0 software package (Sciware, Palma de Mallorca, Spain). A Potentiostate/Galvanostate (PalmSens Instrument BV, Houten, the Netherlands), and the PC Trace software (PalmSens) are used to control the electrochemical cell and to register the analytical signal.

### 2.3. Operating procedure

The operating procedure consists of two steps.

*Manual SPE conditioning.* The SPE is covered with a 150 μL drop of acetate buffer 50 mmol $L^{-1}$ and sodium chloride 50 mmol $L^{-1}$ (pH 4.6) and pretreated at +1.6 V for 120 s followed by 60 s at +1.8 V to eliminate impurities and activate the surface. After drying at room temperature for 24 h, the working electrode is coated with 5 μL of Nafion 0.5% (v/v) and dried at 37 °C for 30 min. A microscope (Motic, Xiamen, China) is used to check the quality of the SPE and to apply the Nafion drop in order to guarantee a homogeneous Nafion film cover of the whole surface of the working electrode.

*Automatic (on-line) BiFE formation and electrochemical determination of Cd.* Table 1 summarizes the general analytical procedure for the automated formation of the BiFE and Cd determination. The procedure is a cycle (loop A) that includes the steps needed to aspirate the sample and reagents, discharge the front and tail of the mixing plug, lead the center of the mixing plug into the flow cell during the electrochemical deposition, stop the flow for Cd stripping and clean the whole system with carrier after every measurement. The volume dispensed in step 7 is directly related to the deposition time, the flow rate and the volume aspirated in step 3. These parameters can be easily modified in order to obtain a better sensitivity. The change of the selection valve position at the beginning of the loop allows building up the standard addition calibration curve.

### 2.4. Sample collection and analysis procedure

One sample of coastal surface seawater from Port de Sóller (Mallorca, Balearic Islands, Spain), was collected and filtered by 0.45 μm with a nylon membrane filter to separate particulate matter. Commercial drinking water was used as purchased. Both samples were acidified at pH 2.0 with HCl 4 mol $L^{-1}$, placed in quartz tubes and UV digested for 2 h using a high pressure 150 W Hg lamp.

Cd determinations obtained by the BiFE-SPE-MSFIA were validated by analysis with a HMDE using a commercial analytical system (663 Stand, Metrohm coupled to a μAutolab, Ecochemie). Two 10 mL aliquots of the sample were acidified (pH 2.0) and UV digested as described above, left to equilibrate overnight, and its Cd concentration determined the next day by SWASV with internal calibration. The analytical accuracy of the HMDE cell was assessed by determination of the Cd concentration in the certified river water SLRS-1 (National Research Council of Canada). The analysis ($0.013 \pm 0.005$ μg $L^{-1}$) showed a good agreement with the certified concentration ($0.015 \pm 0.002$ μg $L^{-1}$).

ICP-MS was used as a second reference method to quantify the Cd concentration in the sample. Cd was pre-concentrated by the APDC/DDDC organic extraction [25] and analyzed by ICP-MS (PerkinElmer ELAN DRC-e). The accuracy of the analysis was established using River Water Reference Material for Trace Metals (SLRS-4, NRC-CNRC) [26]. The analysis of the reference material SLRS-4 (0.012 μg $L^{-1}$) showed a good agreement with the certified concentration (0.013 μg $L^{-1}$).

## 3. Results and discussion

### 3.1. Screen printed electrode conditioning

Before analysis, a pretreated SPE was attached to the flow cell, initial air bubbles were eliminated flushing the system with 0.7 mL $min^{-1}$ of carrier solution and ten cycles of the procedure summarized in Table 1 were performed while passing an 800 μg $L^{-1}$ Bi solution in acetate buffer (50 mmol $L^{-1}$). This process was necessary to bring down the baseline and eliminate the interference in the form of a wide wave at −0.6 V that appears with every new SPE (Fig. S1). This interference was probably due to some impurity present in the Nafion solution or in the carbon ink as it disappears after ten initial cycles. As a result, it was created a Bi layer film that served as a substrate for the posterior Bi and Cd co-deposition during the formation of new films for Cd analysis. BiFEs are not reoxidized and film thickness grows with consecutive analyses because the potential is scanned up to −0.4 V during the stripping and cleaning steps. The increasing Bi substrate was not available for Cd deposition as shown by the lack of trend by replicates at the same Cd concentration (Fig. 3). This behavior is discussed in detail below.

### 3.2. Optimization of the bismuth concentration and flow rate

The Bi concentration was firstly optimized in batch in an acetate buffer solution (50 mmol $L^{-1}$ and NaCl 100 mmol $L^{-1}$)

**Table 1**
Main steps of the AutoAnalysis 5.0 standard analytical procedure for Cd determination BiF-SPE.

| Step | Device | Instruction | Comment |
|---|---|---|---|
| 1 | MSP | Start loop A | Beginning of the determination protocol |
| 2 | SV | Moves to position 1 | Connecting S3 to Std 1 reservoir |
| 3 | MSP | PK 1.300 mL at 4.000 mL $min^{-1}$ (19.5 s) V: [1-Off 2-On 3-On 4-Off 5-Off] | Picking up of sample in HC1 Acetate buffer and Bi and Cd standard in HC2 |
| 4 | SV | Moves to position 5 | Connecting HC2 with the flow network |
| 5 | MSP | DP 0.300 mL at 4.000 mL $min^{-1}$ (4.5 s) V: [1-On 2-On 3-On 4-Off 5-On] | Discarding the front of the mixing plug |
| 6 | MSP | DP 0.200 mL at 0.500 mL $min^{-1}$ (24 s) V: [1-On 2-On 3-On 4-Off 5-Off] | Charging the flow cell |
| 7 | MSP and PalmSens | DP 0.975 mL at 0.4500 mL $min^{-1}$ (130 s) V: [1-On 2-On 3-On 4-Off 5-Off] 30 s at −0.4 V (cleaning) 100 s at −1.4 V (deposition) | Renewing the flow cell with fresh solution during the SPE electrochemical cleaning and deposition period |
| 8 | MSP | Stop the flow | Rest period |
| 9 | PalmSens | SWASV from −1.4 to −0.4 V at 100 Hz pulse 40 mV and step 15 mV | Voltammogram registration |
| 10 | MSP | DP 1.200 mL at 4.000 mL $min^{-1}$ (18 s) V: [1-On 2-On 3-Off 4-Off 5-On] | Cleaning the tubes with carrier |
| 11 | MSP | DP 0.300 mL at 0.500 mL $min^{-1}$ (36 s) V: [1-On 2-On 3-On 4-Off 5-Off] | Cleaning the flow cell with carrier |
| 12 | MSP | PK 1.675 mL at 6.383 mL $min^{-1}$ (15.7 s) V: [1-Off 2-Off 3-Off 4-Off 5-Off] | Filling the syringe to start a new cycle |
| 13 | MSP | End loop A | End of the determination protocol |

SV: selection valve; V: solenoid valve; MSP: multisyringe pump; BiF-SPE-MSFIA: bismuth film on screen printed electrode coupled with Multi Syringe Flow Injection Analysis; PK: pickup; DP: dispense.

spiked with 50 μg $L^{-1}$ Cd. Bi concentrations used were in the range 250–2000 μg $L^{-1}$ and the Cd concentration registered after deposition for 150 s at −1.1 V. At Bi concentrations in the range 500–1000 μg $L^{-1}$ the Cd peak showed an increase to a plateau (Fig. S3) with signal decay and peak broadening at higher concentrations.

The flow rate significantly affects the bismuth film formation in a similar fashion to the effect of the stirrer speed when the electrode is used in batch [27,28]. A multivariate experimental design was used to study simultaneously the flow-rate and the concentration of Bi. For this purpose, a factorial design $3^2$ was applied (factor: flow rate with levels: 0.56 mL $min^{-1}$, 0.63 mL $min^{-1}$, 0.70 mL $min^{-1}$ and factor: Bi concentration with levels: 0.50 mg $L^{-1}$, 0.75 mg $L^{-1}$ and 1.00 mg $L^{-1}$). The maximum peak height (3 replicas corresponding to 50 μg $L^{-1}$ of Cd) was used as dependent variable.

The flow rate and Bi concentration affected significantly the peak height, although there is not significant interaction between them. The optimal values found via the response surface graphic (Fig. S4) were in the middle of the range of study: 800 μg $L^{-1}$ of Bi and 0.63 mL $min^{-1}$ for the flow rate.

### 3.3. Effect of varying the electrochemical parameters

Electrochemical parameters: deposition potential ($E_{dep}$), deposition time ($t_{dep}$), and scan parameters: step potential ($E_{step}$), pulse potential ($E_{pulse}$) and frequency ($f$) were varied in the attempt to optimize the analytical conditions and, at the same time, elucidate the electrode process.

#### 3.3.1. Deposition potential

The effect of $E_{dep}$ on the peak heights of Zn and Cd (25 μg $L^{-1}$) was evaluated in the range −1.2 to −1.5 V in order to obtain better sensitivity and better limit of detection (LOD) (Fig. S5). Zn was selected as a potential source of interferences, since its peak, located at a more negative potential than Cd, can overlap the Cd peak at high Zn concentrations, as was experimentally confirmed. Peak heights increased as the deposition potential shifted to more negative values, reaching a maximum at $E_{dep}$ = −1.45 V. Nevertheless, −1.4 V was selected as optimal $E_{dep}$ due to better resolution and reproducibility of the peaks. The Zn peak appeared at $E_{dep}$ more negative than −1.3 V. At less negative $E_{dep}$ it was possible to determine Cd in samples with high Zn concentrations preventing overlapping with the Cd peak, at a low cost of sensitivity (23% fall).

#### 3.3.2. Optimization of scan parameters: step potential, pulse potential and frequency

The use of pulsed voltammetric techniques as SWASV implies that the scan rate (from $f$ times $E_{step}$) and $E_{pulse}$ have an important effect on the sensitivity. Values of $f$, $E_{step}$ and $E_{pulse}$ found as optimal in the bibliography are around 25 Hz, 5 mV and 20 mV, with higher values reported to cause noise and peak distortion [9,29,30]. In our case, poor Cd signals were obtained with conventional parameters whereas high, sharp and reproducible signals resulted at higher $f$, $E_{step}$ and $E_{pulse}$ (Fig. 2). Crowley and Cassidy found similar results working at high scan rates for a Nafion-coated glassy carbon electrode [31]. A multivariate optimization of the electrochemical parameters was performed on 25 μg $L^{-1}$ of Cd via a factorial design $2^3$. The levels selected were: 5 and 15 mV ($E_{step}$), 20 and 40 mV ($E_{pulse}$), 80 and 100 Hz ($f$), close to the end of the range of linearity. The estimated surface response did not show curvature

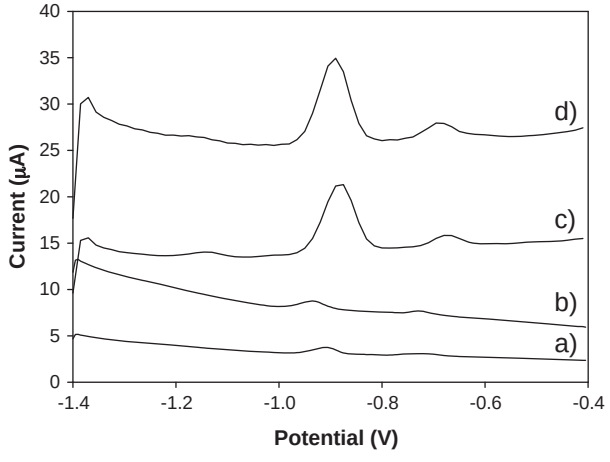


**Fig. 2.** Effect of the scan parameters on the peak height of 10 μg $L^{-1}$ of Cd in acetate buffer (50 mmol $L^{-1}$) at 100 s of $t_{dep}$. Voltammograms at different $f$, $E_{step}$ and $E_{pulse}$: (a) 20 Hz, 5 mV and 20 mV; (b) 20 Hz, 5 mV and 50 mV; (c) 100 Hz, 15 mV and 25 mV; (d) 100 Hz, 15 mV and 40 mV.

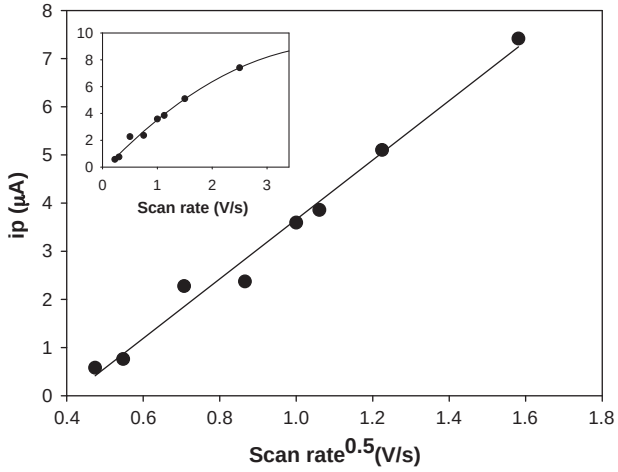


**Fig. 3.** Effect of the scan rate on the peak height of 6 μg L$^{-1}$ of Cd in acetate buffer (50 mmol L$^{-1}$), depositing at −1.4 V for 100 s.

(Fig. S6); however, higher scan rates and $E_{pulse}$ incremented the signal but only a fraction of the increment both caused to the scan baseline. The values selected were: $f$ (100 Hz), $E_{step}$ (15 mV) and $E_{pulse}$ (40 mV), the best compromise among peak height, peak sharpness and baseline.

Fig. 3 shows the effect of the scan rate on the height of the Cd peak. The peak increases in a less-than linear fashion (insert in Fig. 3) that becomes linear when plotted as a function of the square root of the scan rate. This is characteristic of film electrodes that present semi-infinite linear diffusion of the analyte caused by a combination of very fast scan rates with thick electrode films. Semi-infinite linear diffusion is characterized by limited mass transport and the absence of depletion effects in the film [32]. Since the electrode is not reoxidized in between replicates, and there is no Cd depletion from the BiFE, the absence of Cd carry over to the next measurement had to be tested by continuous analysis of the same sample. Fig. S2 shows the successive peak heights recorded during a working day for the analysis of 6 μg L$^{-1}$ Cd in acetate buffer (50 mmol L$^{-1}$, pH 4.6) proving the stability and reproducibility of replicates using the same SPE (1.5% of RSD). The lack of significance of the slope confirm the lack of trend of the data: $i_p$(Cd) = (0.003 ± 0.01)[Cd] + (5.19 ± 0.06), $R$ = 0.0109.

### 3.3.3. Deposition time

The effect of the $t_{dep}$ on the peak height of 50 μg L$^{-1}$ Cd was studied using the BiFE in batch. The maximum Cd peak height was observed at 250 s, with longer times causing a decrease of the signal. A similar behavior was reported before [33].

The $t_{dep}$ range that can be studied in flow was limited since the volume restriction caused by the use of syringes. There is a non-linear relation between $t_{dep}$ and the peak height of Cd in the range 0–200 s (Fig. S7). This effect is caused by the presence of Bi in the analyte solution that increases the thickness of the electrode at longer deposition times and therefore the Cd mass plated is not proportional to the $t_{dep}$ and the distribution fits a second order polynomial equation ($R^2$ = 1.000). The $t_{dep}$ selected was 100 s as a best compromise between sensitivity and frequency of analysis, but in some samples Cd was deposited at 200 s to improve the LOD.

## 3.4. Interferences

BiFEs are prone to fouling by surface-active compounds that cause deactivation of the electrode surface. Signal depression can be avoided by restricted diffusion of macromolecules through the Nafion layer. Because analyte deposition is carried out at a mild acidic pH (4.6), a second effect that organic matter can cause is a restriction of the metal lability due to complexation. Aliquots of seawater were UV digested to destroy the organic matter and assure that all interferences were due to inorganic compounds. No differences were found in the measurement of Cd in water samples with and without UV digestion. This reproducibility suggests that both processes: electrode surface fouling and metal complexation, were negligible in the analytical conditions.

$Cu^{2+}$ ions can suppress the peak intensity by intermetalic formation [34,35]. However, this interference only occurs at Cu concentrations higher than common levels in fresh and marine waters [4]. A quick test of the Port de Soller sample by ASV on the HMDE after UV digestion and 24 h acidification to pH 2 gave a concentration of 0.5 μg L$^{-1}$. Since sensitivities found for both natural samples were very close (0.46 and 0.49 μA μg$^{-1}$ L respectively), we assumed that copper concentrations in drinking water were not significantly higher than the Cu concentration found in seawater.

At the deposition potentials used in this work, Pb and Zn are also co-plated on the BiFE, being a potential source of interferences. As indicated above, high levels of $Zn^{2+}$ can overlap the Cd peak. This interference was solved preventing the plating of Zn using −1.2 V as deposition potential. Pb did not interfere on the determination of Cd: the linearity and sensitivity of the calibration curve for Cd in acetate buffer were not affected by 100 μg L$^{-1}$ Pb ($i_p$(Cd) = 0.141[Cd] − 0.08, $R^2$ = 0.9997 at 30 s of deposition time). Additions of Pb up to 1000 μg L$^{-1}$ did not affect the reproducibility of the peak caused by 20 μg L$^{-1}$ Cd (at 30 s of deposition time, $i_p$ = 2.8 ± 0.1 μA, 3.6% RSD).

## 3.5. Analytical performance

There is variability in the sensitivity of the Cd response from different SPEs due to small variations caused by manual operations during their manufacture and conditioning. The sensitivity of the Cd signal for different SPE could vary by a factor of two (whole range: 0.96–0.43 μA μg$^{-1}$ L; $t_{dep}$ = 100 s). For each single SPE, the Cd sensitivity was determined and remained stable for its whole life span, as was mentioned above and shown in Fig. S2. The suitability of cleaning time and cleaning potential were proved by analysis of a blank immediately after the analysis of a 60 μg L$^{-1}$ Cd, showing that any memory effect was negligible.

The analytical performance of the BiF-SPE-MSFIA system was evaluated by examining the linear range, precision, detection limit and sampling frequency in acetate buffer (50 mmol L$^{-1}$; pH 4.6) at −1.4 V $E_{dep}$. The RSD evaluated by ten repetitive determinations of 6 μg L$^{-1}$ Cd in acetate buffer was 1.59%. The linear behavior was confirmed up to 60 μg L$^{-1}$ Cd for different deposition periods. The 3× standard deviation of ten replicates for the analysis of 4 μg L$^{-1}$ Cd at 200 s of $t_{dep}$ gave a LOD of 0.79 μg L$^{-1}$. The measurement frequency, defined as the number of scans per hour, was 14 h$^{-1}$. It was achieved with low solution consumption (1.3 mL per measure at 100 s of $t_{dep}$).

## 3.6. Cd determination in natural samples

The proposed method was applied to the direct determination of Cd in two different water samples: coastal seawater from Port de Sóller (Mallorca, Spain) and bottled mineral drinking water. Totally automatic on-line standard addition was used to calibrate the response. Fig. 4A and B shows SWASV scans obtained during the determination and calibration for both samples (seawater: $i_p$ = (0.46 ± 0.01) × [Cd] + (0.09 ± 0.26), $R^2$ = 0.9986; mineral water: $i_p$ = (0.49 ± 0.02) × [Cd] − (0.07 ± 0.05), $R^2$ = 0.993). Good linearity and reproducibility were observed but Cd concentrations could not be determined. Both Cd concentrations were examined by ASV

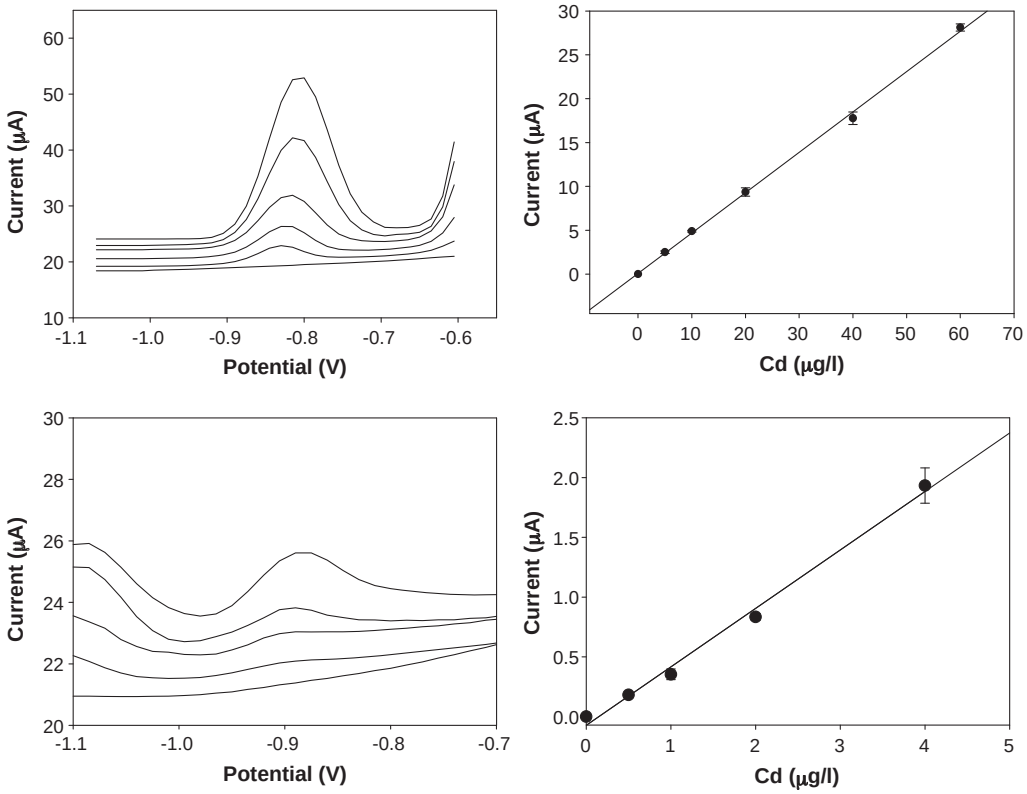


**Fig. 4.** On-line standard addition curves and voltammograms over waters samples: (A) Portĭd Sóller seawater sample and (B) mineral drinking water samples.

**Table 2**
Summary of Cd determination in samples by online standard addition and add-recovery test.

| Sample | Procedure | Original ($\mu g L^{-1}$) | Add ($\mu g L^{-1}$) | Found ($\mu g L^{-1}$) | Rec % | RSD % |
|---|---|---|---|---|---|---|
| Mineral water $t_{dep}$ = 200 s | MSFIA | <LOD | 20 | 19.8 | 99 | 2.7 |
| | HMDE | 0.37 ± 0.01 | | | | |
| | ICP-MS | 0.43 ± 0.01 | | | | |
| Seawater $t_{dep}$ = 200 s | MSFIA | <LOD | 20 | 20.3 | 101.4 | 2.1 |
| | HMDE | 0.095 ± 0.020 | | | | |
| | ICP-MS | 0.026 | | | | |

**Table 3**
Comparison of analytical performances of SW-ASV determination of Cd, on a Bi electrode coupled with a flow system.

| Ref. | Flow system | Electrode | Measure frequency[d] | LOD ($\mu g L^{-1}$) | Volume of reagent/S (mL) | $t_{dep}$ (s) |
|---|---|---|---|---|---|---|
| [36] | SI-LOV | BiFE on Nafion-coated GCE[a] | 22 | 0.88 | 1.7 | 100 |
| [37] | SIA | BiFE on carbon nanotubes-modified | 14 | 0.8 | 2.160 | 180 |
| [9] | FIA-SIA | BiFE on GCE and on Nafion-coated | 11[b] | 2.0 | 1.000 | 180 |
| [38] | SIA | BiFE on Nafion-coated GCE | 15[c] | 2.0 | 0.600 | 120 |
| [39] | Microfluidic channel | Microchip Bi electrodes | 20 | 9.3 | 0.010 | 90 |
| In this work | MSFIA | BiFE on Nafion-coated SPE | 14 | 0.79 | 1.300 | 100 |

[a] Using linear sweep anodic stripping voltammetry.
[b] Calculated by this table.
[c] Calculate by Table 1.
[d] Number of scans per hour.

on a HMDE. Table 3 shows that Cd concentrations in the samples are below the LOD of the BiF-SPE-MSFIA. Nevertheless, Fig. 4 demonstrates that the Cd concentration in water samples can be determined accurately by the proposed system at Cd concentrations well below the limit stipulated by the European directive ($5 \mu g L^{-1}$). In order to test the analytical accuracy of the BiF-SPE-MSFIA, both samples were spiked with $20 \mu g L^{-1}$ of Cd and recalibrated to determine the recovery. High recoveries of 99.0 and 101.4% were obtained for drinking water and seawater respectively (Table 2).

## 4. Conclusions

In this work, we present for the first time the analysis of Cd in natural waters using a system constituted by a newly developed BiF-SPE coupled to an automated MSFIA via a homemade flow cell. The high sensitivity of SWASV combined with the MSFIA allowed the use of small quantities of reagents and sample, provided higher sample throughput of analysis and made possible the automatic determination of Cd in natural waters at lower levels than limits established by European directives. The designed

flow cell, with a very small volume, minimized the dead volume reducing the consumption of reagent and sample. This cell allowed an easy replacement of the SPE, and together with the small size of the syringe module, selection valve, and the PalmSens potentiostate, offers the possibility to use the BiF-SPE-MSFIA as a portable device, adequate for on-board measurement in marine campaign and in situ monitoring of Cd.

A comparison between the analytical performance of electrochemical systems previously proposed for the on line determination of Cd and our work is summarized in Table 3. The first method is based on the use of a glassy carbon electrode placed in a Lab-on-Valve system, which makes difficult the conditioning of the working electrode, the second one requires larger sample volumes, and the rest of the methods have worse detection limits than our system. Our LOD is in line with the bests in Table 3.

Summarizing, analysis of these three parameters combined shows that our system presents the better balance: the lowest LOD ($0.79\ \mu g\ L^{-1}$), good sample throughput ($14\ h^{-1}$) together with low consumption of reagents and sample (1.3 mL). Summarizing, the BiF-SPE-MSFIA is an excellent automatic system for the laboratory or field determination of Cd in natural samples due to its accuracy, precision, low cost, and low toxicity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2012.01.032.

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