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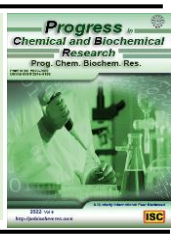

Original Research Article

Revising Flow-Through Cells for Amperometric and Voltammetric Detections Using Stationary Mercury and Bismuth Screen Printed Electrodes

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HIGHLIGHTS

- Several flow cells using a stationary mercury electrode for amperometric an anodic stripping voltammetric detection have been compared
- Two bismuth screen printed electrodes have been developed for Cd (II) and Pb (II)
- The flow cells for the screen-printed electrodes have considerably reduced the needed volumes of reagents and samples.
- The developed automated system can be very useful for monitoring tasks in fieldwork and on-board measurements.

ABSTRACT

Heavy metals 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 two multisyringe flow analysis (MSFIA) procedures to determine Tl(I) Pb(II), In(III), and Cd(II) using four homemade flow cells for amperometric and anodic stripping voltammetric detection using a stationary mercury electrode (SMDE), and another two using bismuth screen printed electrodes for Cd(II) and Pb(II). In all cases, a differential pulse polarographic system has been used. The control of the whole process has been carried out with a personal computer and the AutoAnalysis program. The Cd determination in drinking water has been assessed using the anodic stripping variant, which has allowed carrying out analyses with very low sample consumption, unable to be manipulated using batch methods. The detection limit for a sample of 200 µL was of 2.3 µg L^{-1}, which in terms of absolute analyte amount corresponds to 450 picograms. The use of screen-printed electrodes in MSFIA, together with the small volume of the flow cell and the reduced surface area of the solid phase electrode (SPE) have considerably reduced the volume of reagents and samples to be used. The Bi use is one of the most important advantages of this system, since it is a recognized substitute for Hg, and its impact on the environment is much lower due to its reduced toxicity.

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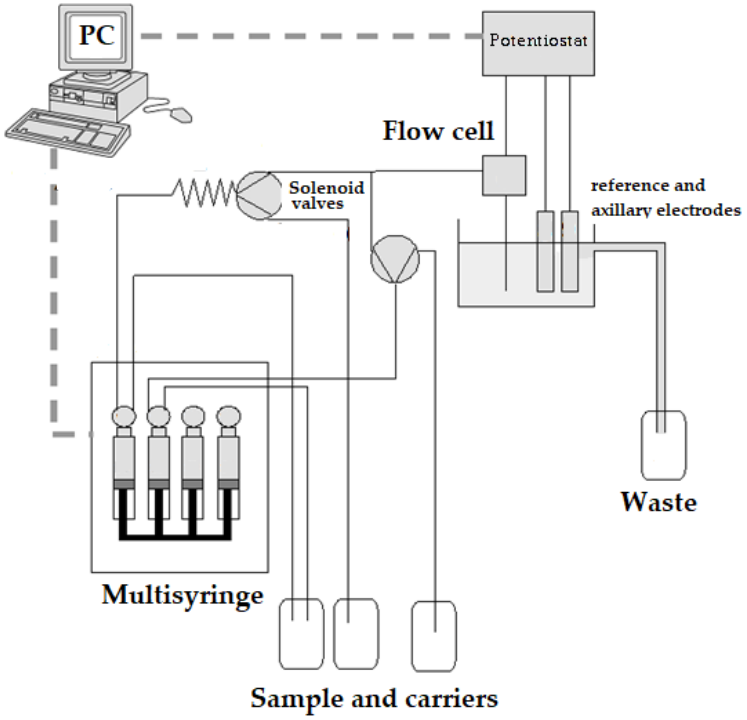
GRAPHICAL ABSTRACT



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 [1], in metallurgy, and electronics processes.

The spectrometric techniques such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Optical Emission Spectrometry, or Mass Spectrometry (ICP OES 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, the electrochemical techniques require small, low-cost instruments, which can be portable to the field for in situ analysis and offer very low limits of detection without sample preconcentration.

Flow techniques present great versatility in the automation and decrease of analysis time [5]. One of the flow methods is multisyringe flow injection analysis (MSFIA), which uses a multisyringe burette as a liquid driver which may be coupled with up to 4 syringes [6,7].

Electroanalytical methods have been employed in the detection of different flow species, among them the amperometric detection using different working electrodes [8,9]. In spite of the many efforts undertaken to substitute mercury as an electrode material [10], mainly due to its toxicity, up to date very few materials have proved to offer the set of advantages attributed to mercury as a working electrode material [11].

It is also well-known that non-scanning direct current amperometric techniques do not present a great resolutive power in the detection or

determination of analyte mixtures. Nevertheless, it is very useful in some particular cases, such as in the determination or detection of dissolved oxygen using the Clark electrode [12,13]. Moreover, the amperometric detection of mixtures of different analytes, which are electroactives under working conditions with direct current using mercury electrodes, can cause several inconveniences. Another inconvenience is the additivity of intensities. Thus, the detection in a relatively simple way of the more easily reducible analyte in a certain mixture is feasible. The remaining analytes can be theoretically determined by subtraction of intensities, which can easily lead to the accumulation of errors, the greater, the larger the number of analytes.

Amperometric detection using the differential pulse mode overcomes some of the difficulties appearing when using the direct current modality. In this way, the detection or determination with a lower interference of the dissolved oxygen, together with the simultaneous determination of several analytes in mixtures is feasible among others [14,15,16].

To improve the limits of detection different ways of preconcentration of the analytes have been used prior to their final flow determination. One of the preconcentration variants which can be used in flow methods, almost directly, is based on the concentration of the analyte over some suitable electrode inside the flow cell [7,17,18,19,20].

Particularly, in the case of the stripping methods, the differential pulse technique offers better limits of detection in the final determination than classical linear scanning techniques. Problems associated with the noise presence due to the liquid movement, especially when using the stationary mercury drop electrode (SMDE), are minimized using different ways of attenuating the pulses [**Error! Bookmark not defined.**] originated by liquid drivers (peristaltic pumps, piston burettes, etc.), being the stop flow scanning modality preferred.

For the detection or determination of flow analytes we have tested in this paper different kinds of flow cells, both commercial or constructed by ourselves [21-26]. In the present work, the behaviour of 6 homemade flow cells was studied, four for mercury hanging electrodes and two for screen printed electrodes.

In this paper, we have used screen printed electrodes in MSFIA, together with the small volume of the flow cell and the reduced surface area of the solid phase electrode (SPE) to considerably reduce the volume of reagents and samples. The Bi application is one of the most important advantages of this system, since it is a recognized substitute for Hg, and its impact on the environment is much lower due to its reduced toxicity. The fact of being an automatic system, the low cost of its components, its simplicity, and ease of handling, make it a system that could be useful for monitoring tasks in fieldwork, or measurements on-board.

2. Experimental

2.1. Reagents and solutions

For mercury electrodes

Deionized water was obtained from a Millipore Corporation (Billerica, MA, USA) apparatus. All reagents employed were of analytical grade. Hydrochloric acid 0.1 mol L^{-1} solution was prepared by adequate dilution with deionized water from 37% m m^{-1} HCl (1.19 g mL^{-1}) (SCHARLAU). Solution of HCl 0.01 mol L^{-1} was prepared by dilution of the former with deionized water. Sodium hydroxide 2 mol L^{-1} solution was prepared by dissolution of the solid (MERCK) in deionized water. The 10^{-3} mol L^{-1} mother solutions of the studied metallic ions were prepared from the following salts: $TlNO_3$ (SUPELCO), $Pb(NO_3)_2$, (MERCK), $CdCl_2$ (MERCK), $InCl_3$ (MERCK) in one of the HCl suitable solutions. The 4 ions working solutions and their

mixtures were prepared by dilution of the former in the adequate medium. Metallic mercury from Almadén (Spain), treated with nitric acid and bidistilled, was used.

For screen printed electrodes

Metal solutions were prepared by diluting Bi(III), Cd(II) and Pb(II) standard solutions (AAS grade, Scharlau). HCl 0.01 mol L^{-1}, 1 mol L^{-1} and 4 mol L^{-1} solutions were prepared by diluting concentrated HCl (32%, Fluka). Two acetate buffers (350 mmol L^{-1} and 50 mM) were prepared by dissolving an equimolar quantity of sodium acetate (Fluka Analytical, TraceSelect) and sodium chloride (Scharlau, reagent grade ACS). The pH value was adjusted to 4.6 with HCl 4.0 mol L^{-1} additions. Nafion (5% wt/vol solution in a mixture of low weight aliphatic alcohol and water, Aldrich Chemicals) were diluted until 0.5%. Artificial reconstituted seawater was prepared according to (APHA, et al., 1992) with analytical grade reagents (Scharlau). HCl 0.01 mol L^{-1} was employed as carrier. 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

For all electrochemical measurements using mercury electrodes, an AMEL Polarographic Analyzer (Model 433) was used. A stationary mercury drop electrode from the same manufacturer (AMEL) constructed with a glass capillary of 135x6 mm, bore 0.1 mm, was employed as a working electrode. A Ag/AgCl electrode (CRISON, Alella, Spain) was used as reference and a Pt electrode (CRISON) as an auxiliary.

All the experiments with screen printed electrodes were carried with a MSFIA system using a PalmSens potentiostat (Palm Instrument BV, Houten, the Netherland http://www.palmsens.com) controlled by the PC Trace software. This PC was further used to manage the electrochemical parameters, and to obtain and handle the analytical signal.

The multi-element (Cd(II) and Pb(II)) stripping was carried out from -1.4 V to -0.4 V. Before starting the measurement, around 5 blank were obtained with the indicated electrochemical conditions using an acetate buffer 50 m mol L^{-1} pH 4.6 with Bi (III) 750 µg L^{-1}. This step makes possible the stabilization of the Bi film and minimizes the residual current, the baseline becoming more horizontal. This assesses the proper functioning of the sensor.

A multisyringe burette (CRISON), provided with one or two additional three-way solenoid valves (Bio-Chem Valve Inc^2., Boonton, New Jersey, USA, http://www.bio-chemvalve.com) was used as a liquid driver.

2.3. Flow-through cells for mercury electrodes

The different flow cells studied all constructed in polymethylmetacrylate (PMMA), are displayed in Figure 1.

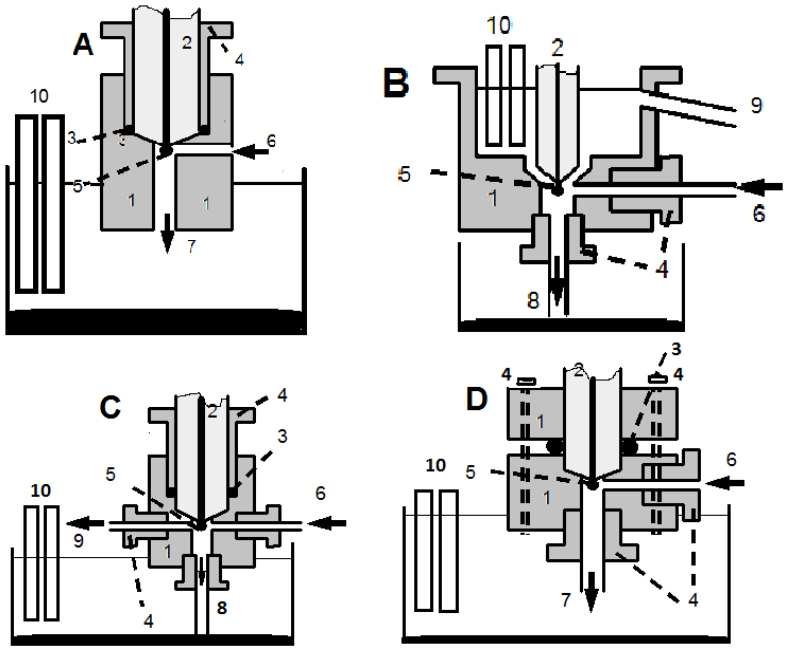


Fig. 1. View of four tested flow-through cells. (1) PMMA Cell body, (2) glass capillary of the SMDE, (3) o-ring, (4) fixation screw, (5) mercury drop, (6) solution inlet, (7) solution and mercury outlet, (8) mercury outlet, (9) solution outlet, and (10) auxiliary and reference electrode

- **Flow cell A** was constructed with a PMMA cylinder of 15 mm of external diameter and a total height of 23 mm. A small side hole of 1.5 mm diameter was drilled to which a tube of 0.5 mm was glued to introduce the solution into the flow cell. A hole less than 3 mm diameter was drilled to allow removing the solution and the mercury used, and thus allowing the electric contact of SMDE with the two remaining electrodes placed in an outside container. SMDE was fixed to the flow cell through a hole drilled in the top, being adjusted with an O-ring and a security screw to avoid liquid leakage. In this case, the flow cell is working immersed inside the liquid in the lower container.
- **Flow cell B** was constructed in such a way that it could be fitted in the same place of the standard flow cell from the manufacturer of the 433 AMEL Polarographic Analyzer, and thus allowing to fit the two remaining electrodes directly inside the flow cell (in this case those from the Polarographic Analyzer manufacturer, using as an auxiliar electrode a Pt wire of 1 mm diameter and 7 mm long and a Ag/AgCl electrode as a reference). The flow cell was made of PMMA with the following measures: external diameter 35 mm, internal diameter 30 mm, top edge diameter 60 mm, total height 40 mm. Alike the remaining studied models, the liquid enters laterally. However, unlike them, the movement of the liquid surrounding the SMDE is upwards. Besides, the glass capillary is found to be separated from the flow cell body. The mercury already used, goes out through the bottom hole, the liquid coming out from the top takes place through the top side tubing. To avoid the liquid coming out from the bottom, a mercury siphon inside the bottom outlet tubing is used.
- **Flow cell C** was constructed from a PMMA block of 20x20 mm and 28 mm high. The SMDE is fitted into the top hole with the aid

of an O-ring and a fixing screw. The side holes, of 1.5 mm diameter each, allow the flow entering and coming out through tubes with fixing screws. The bottom hole plays the same role as that of flow cell B. The two remaining electrodes were placed inside the outside container.

- **Flow cell D** was composed of two PMMA blocks[Error! Bookmark not defined.]. Flow enters through the side hole and comes out, together with the mercury, through the bottom hole, to an outside container, in which the two remaining electrodes are also placed. Its construction is robust and the capillary remains firmly fixed to the flow cell body.

The previous experiments were carried out with the 4 flow cells. In the case of flow cells A and C, the quality of the results obtained (elimination of air bubbles, reproducibility, and robustness) was lower than those obtained with flow cell D. Flow cell B can be used with excellent results in amperometric detection, but not in methods including previous accumulation for a stripping analysis with the proposed procedure. For this latter case, it is exceedingly open and susceptible to the mixing of the solution contained in the flow cell, by either diffusion or convection. Thus, in workflow cell D was used for further experiments.

The used manifold for the mercury electrodes is depicted in Figure 2. The poly (tetrafluoroethylene) tubing was of 0.5, 0.8 and 1.5 mm internal diameter. For instrumental control, data acquisition and processing the AutoAnalysis 5.0 software developed by our research group [27] was employed.

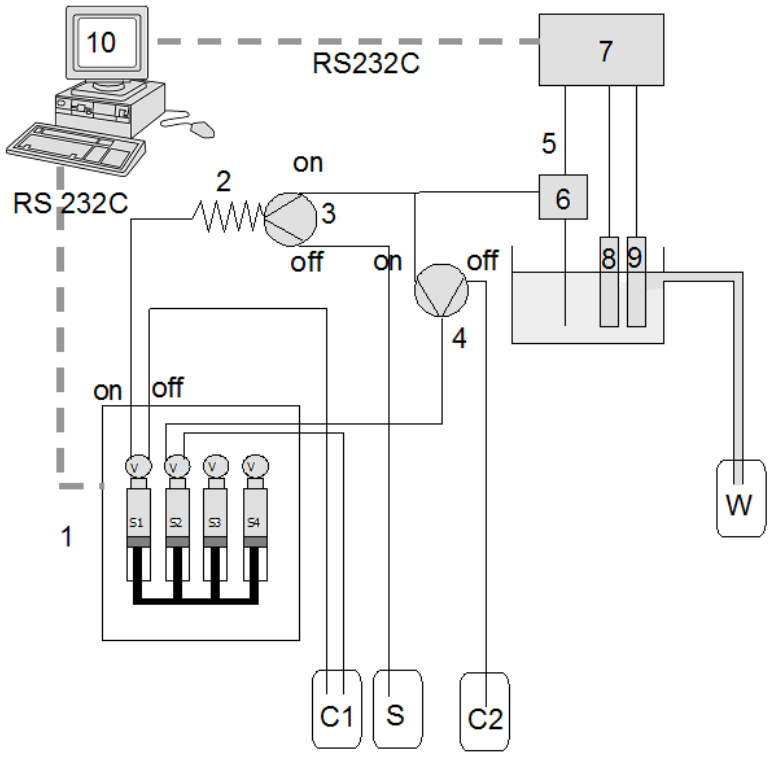


Fig. 2. Diagram of the manifold. (1) multisyringe burette, (2) holding coil, (3) and (4) three-way solenoid valves, (5) SMDE, (6) flow-through cell, (7) potentiostat, (8) reference electrode, (9) auxiliary electrode, and (10) personal computer, (W) waste, (S) sample, (C1) Carrier, and (C2) Carrier or NaOH ; (- - -) RS232C connections; S1, S2, S3, and S4 syringes; V three-way solenoid valve

In our work, only two (S1 and S2) of the four burette syringes available were used. Syringe S1, together with solenoid valve 3, allows picking and further dispensing the sample toward the flow-through cell. Syringe S2 was used to dispense the carrier (support electrode). Solenoid valve 4 allows the on-line addition of a reagent if required. C1 represents the container with the carrier (support electrolyte), C2 the container with 2 mol L^{-1} NaOH or carrier (according to the experiment carried out).

2.3. Flow-through cell for screen printed electrodes

The flow cell, specific for screen-printed electrodes, has been built in our research group. A diagram this cell is shown in Figure 3A, together with a photograph of it, Figure 3B. The cell consists of two pieces of PMMA. In this way, the upper part acts as a screw with two channels that lead the liquid to be analyzed. An o-ring of 8 mm internal diameter and 12 mm od is placed on the bottom of the screw, which allows the electrochemical cell to close tightly. In this way, the three electrodes are confined within a very small volume of 15 µL. The used manifold for screen printed electrode is depicted in Figure 3.

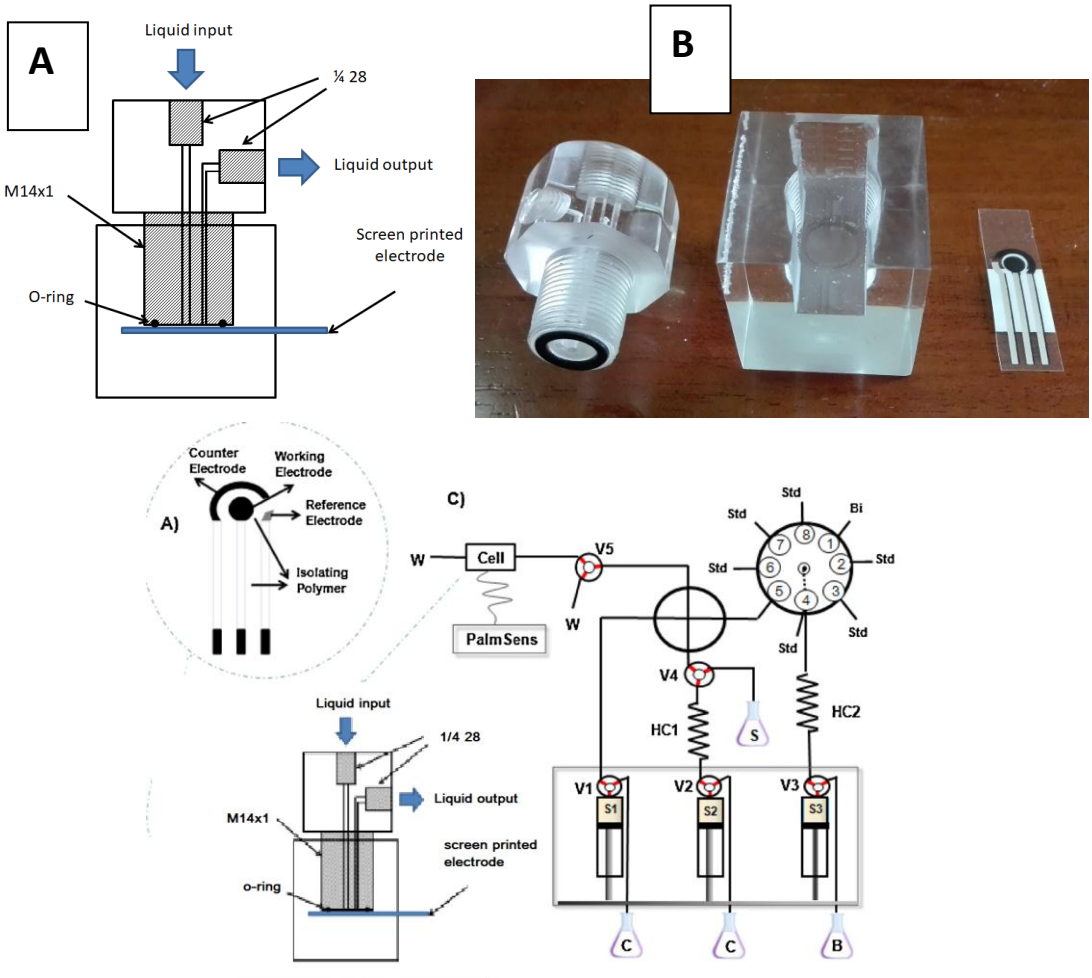


Fig. 3. A) Schematic representation of the flow cell and B) Photo of home-made components of the flow cell, including the screen printed electrode.

2.5.Amperometric detection

2.5.1. Assessment of the system performance

To assess the equipment performance, previous amperometric detection experiments in both direct current (DC) and differential pulse voltammetry (DPV) modes were carried out, taking Cd(II) as a reference element.

The procedure used was as follows: A predefined sample volume of 3.10^{-3} mol L^{-1} Cd was taken with valve 4 in the "off" position and dispensed toward the flow-through cell at a flow rate of 1 mL min^{-1}. A volume of 1 mL was enough to achieve the total passing of the sample. Detection in the DC mode was carried out at -650 mV, whereas an initial potential of -500 mV and pulse amplitude of -60 mV were selected for the DPV mode.

The results obtained in the study of the variation of the Cd(II) signal in relation to the electrode area (DC mode) and the sample volume (DPV mode) are given in Figures 4 and 5. As can be seen in these figures, the system's behaviour is adequate.

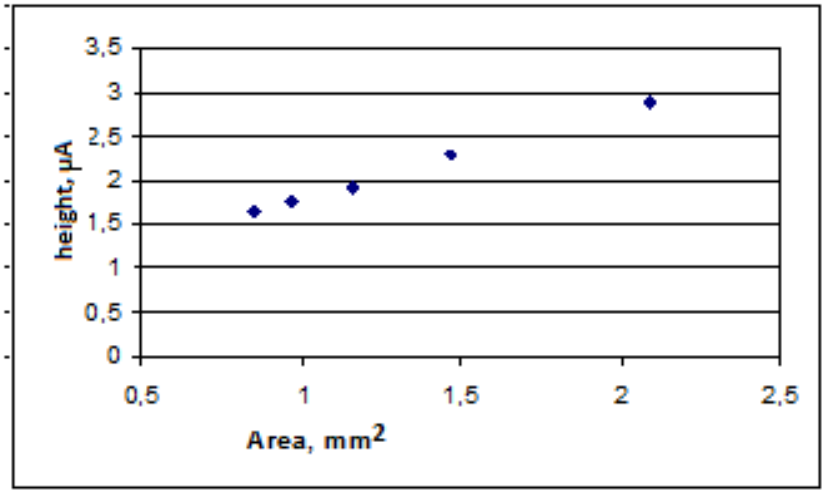


Fig. 4. Influence of the electrode area on the height of the analytical signal of 3.10^{-3} mol L^{-1} Cd(II) in 0.01 mol L^{-1} HCl. Sample size 100 µL. DC mode.

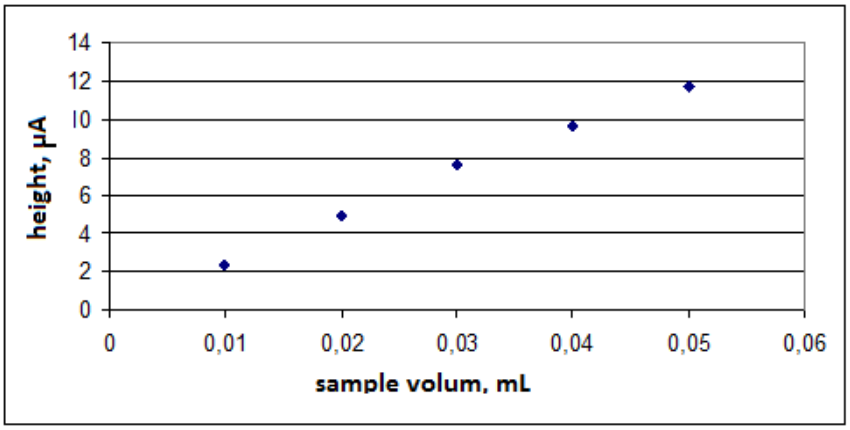


Fig. 5. Influence of the sample volume on the height of the analytical signal of 3.10^{-3} mol L^{-1} Cd(II) in 0.01 mol L^{-1} HCl. Electrode area 1.16 mm^2. DPV mode.

2.5.2. Amperometric detection of Tl(I), Pb(II) and In(III) using mercury electrodes

In previous experiments, the possibility of detecting these ions during the flow through the cell was studied. Values of the parameters, which enable the detection (initial potential, pulse amplitude, pulse duration, current measuring time in each pulse, electrode area, flow rate, sample size, electrode area, etc.) were determined.

It is well-known that separation of the Tl(I) and Pb(II) signals in most acid media is not possible due to the proximity of the half-wave (or peak) potentials. Nevertheless, in 1 mol L^{-1} NaOH medium, the potential at which the Pb(II) signal happens to appear is shifted towards negative values large enough to achieve determination of both elements separately owing to the formation of plumbite. In(III) signal is also shifted toward large enough negative potentials. However, it does not interfere in the Pb(II) determination.

The procedure was the following: detections for each ion by means of potential pulses from the initial pulse up to the complete passing of the sample (S) through the flow cell were carried out sequentially (an injection and a new mercury drop for each ion) in the following way: A sample volume of 70 µL was taken and dispensed with the carrier (S1, C1, 0.01 mol L^{-1} HCL) toward the flow mixing cell, with the aid of valve 4, equal volumes of sample-carrier with 2 mol L^{-1} NaOH (S2 and C2) at a flow rate of 1 mL min^{-1}. The flow rate reaching the cell was of 2 mL min^{-1}. A volume of 1 mL is large enough to attain the total passing of the sample and allow the current to go back to its initial value. The potentials and amplitudes used in each case were the following:

- Tl(I): Initial potential -380 mV, pulse amplitude -80 mV,
- Pb(II): Initial potential -666 mV, pulse amplitude -80 mV,
- In(III): Initial potential -1012 mV, pulse amplitude -80 mV

Figure 6 demonstrates a flowgram corresponding to the detection of these three ions in a mixture.

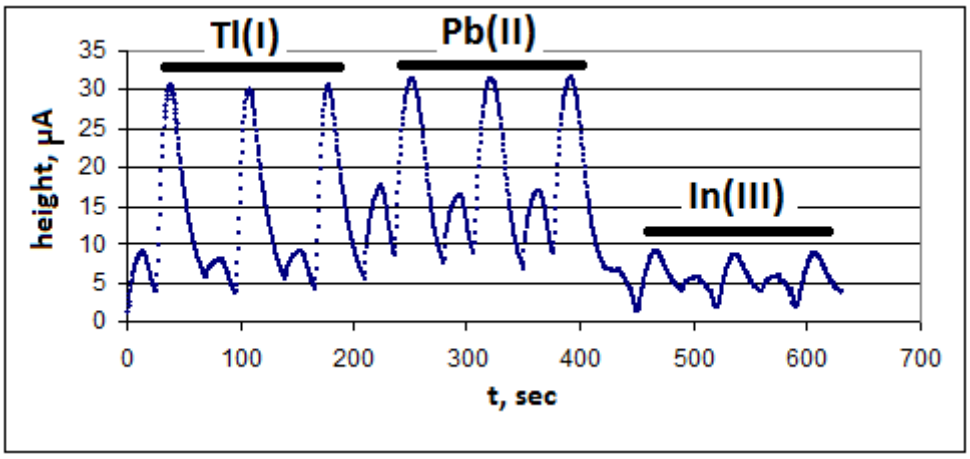


Fig. 6. Consecutive amperometric detection of Tl(I), Pb(II), and In(III). Sample size 70 µL, electrode area 1.02 mm^2. Ions concentrations: Tl(I) $6.4x10^{-3}$ mol L^{-1}, Pb(II), and In(III) $8x10^{-3}$ mol L^{-1}. DPV mode. Tl(I): Initial potential -380 mV, pulse amplitude -80 mV; Pb(II): Initial potential -666 mV, pulse amplitude -80 mV; In(III): Initial potential -1012 mV, pulse amplitude -80 mV.

Calibration curves with fairly good linearity were obtained with correlation coefficients higher than 0.998 and limits of detection was of $1.8x10^{-4}$ for Tl(I), $1.6x10^{-4}$ for Pb(II) and $1.9x10^{-4}$ mol L^{-1} for ln(III). A number of different concentrations

of these three ions between 2 and 20x10^{-4} mol L^{-1} were tested with a sample size of 20 µL.

It should be noted that under the above-mentioned conditions, the noise caused by the liquid movement is important. Therefore, the use of procedures allowing stop flow measurements is preferred.

2.5.3. Amperometric detection of Cd(II)

To achieve better limits of detection, Cd(II) was selected as a reference element and different variants of the anodic stripping method were used obtaining voltagrams with the stop flow differential pulse mode. Before proceeding to the study of the modes involving accumulation, the behaviour of the variation of the Cd(II) signal as function of the accumulation time was studied under the geometric conditions of the used flow cell (Figure 1D). Thus, 2 mL of sample of a solution of 6x10^{-6} Cd(II) in 0.01 mol L^{-1} HCl were taken and 1.5 mL were further dispensed towards the flow cell, in such a way that the Cd(II) concentration of the solution contained in the flow cell happened to be the same as that of the sample. Under these conditions, in the stop flow mode, the variation of the Cd(II) signal was studied vs. the accumulation time. The results are depicted in Figure 7.

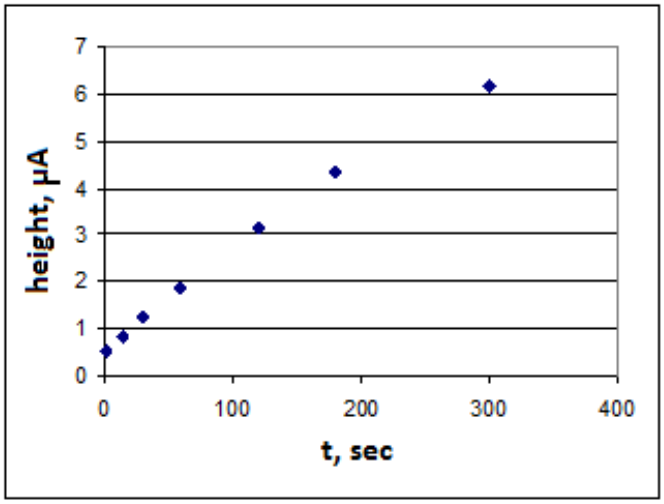


Fig. 7. Variation of the analytical signal with accumulation time for 6x10^{-6} mol L^{-1} Cd in 0.01 mol L^{-1} HCl. Electrode area 1.16 mm^2. DPV mode. Accumulation potential -700 mV, pulse amplitude 50 mV, scanning speed 25 mV s^{-1}, pulses duration 100 ms.

Several variants were studied for the previous electrolysis process:

- Accumulation during the continuous flow of the sample through the cell, and stop flow during stripping.
- Accumulation in stop mode when the maximum analyte concentration was attained in the cell, and stop flow during stripping.
- Accumulation during the flow of the sample through the cell in successive stop-wait-flow mode from the beginning of the appearance of the analyte signal (previously determined by amperometric detection).

This latter variant presents several advantages over the first two and over another proposal**Error! Bookmark not defined.** based on the continuous recirculation of the sample for a long period of time through the flow cell during accumulation. These advantages are based on the following aspects:

1. It is possible to determine, for each cycle, the appropriate waiting time to be able to work

within the zone where the analytical signal happens to be linear in relation to the accumulation time. This time will be mainly dependent on the geometric characteristics of the flow cell. During this waiting time, in each cycle, most part of the accumulation process is undertaken. In each cycle the flow cell content is renewed, totally or partially, with fresh solution, and thus making the accumulation process more efficient.

2. The accumulation process is carried out both during the stop flow and during the movement of the liquid which renews the solution in the cell flow.

Obviously, when using the proposed cyclic stop-wait-flow procedure, it is also possible to carry out, if required, a change of the medium to undertake the stripping step. The sequence used for the Cd(II) determination is listed in Table 1.

Table 1. Analytical procedure used for Cd(II) determination

Step	Operation	Flow rate (ml min^{-1})	Positions of the solenoid valves (Fig. 1) V1	V2	3	4	Description
1	Dispense 0.700 Ml	15.0	On	On	On	On*	Preconditioning the system
2	Pick up 0.200 mL	1.5	On	Off	Off	Off	Picking the sample
3	Dispense 0.540 mL	1.0	On	Off	On	Off	Beginning of the Cd(II) signal
4	Conditioning the polarographic analyser, beginning the electrolysis	-	-	-	-	-	Change the electrode surface, setting the electrolysis, and stripping step conditions, potential at -700 mV.
5	Beginning Loop	-	-	-	-	-	Accumulation loop
6	Wait 30 sec	-	-	-	-	-	Accumulation
7	Dispense 0.002 mL	1,0	On	Off	On	Off	Solution slow renewing during accumulation
8	Loop	-	-	-	-	-	Repeat 16 times from step 5
9	Stripping step	-	-	-	-	-	Obtaining the voltagram
10	End measuring	-	-	-	-	-	Voltagram obtained
11	Dispense 1.500 mL	15.0	On	On	On	On*	Cleaning the system

* In this procedure, valve 4 was used for speeding up the cleaning of the system.

The proposed procedure was tested by obtaining a calibration curve (Figure 8) and the determination of Cd(II) in spiked tap water.

The calibration curve obtained when adjusting the peak height as a function of the concentration is $y = -0.0151 + 0.250\times10^{7}X$, and is applicable between 0.8 and $8x10^{-7}$ mol L^{-7} of Cd(II) in 0.1 mol L^{-1} HCl, with a linear correlation coefficient of 0.998.

Results corresponding to the accuracy of the procedure are shown in Table 2.

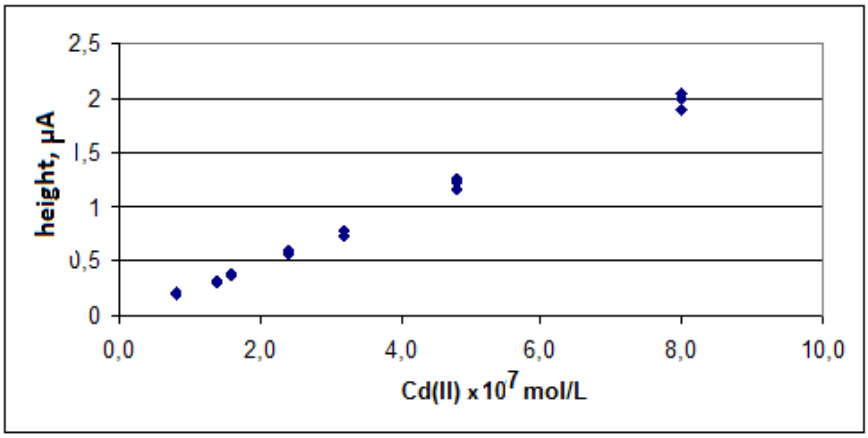


Fig. 8. Calibration curve for Cd(II) in 0.1 mol L^{-1} HCl using the procedure described in Table I.

Table 2. Evaluation of the accuracy for Cd(II) determination

Added, µg	Recovered, µg	% recovery
0.135	0.136	100.7
0.135	0.130	96.3
0.135	0.135	100.0
0.135	0.128	94.8
0.135	0.143	105.9
0.135	0.133	98.5

Precision expressed as relative standard deviation (RSD) = 0.039%

With the modality proposed in the present work, i.e. cyclic stop-wait-flow, a limit of detection (LOD) was of 20 nmol L^{-1} (or 2.3 µg L^{-1}) was obtained for Cd(II), with a sample of 200 µL, thus detecting a mass of 450 picograms. Similar limits of detection have been reported[Error! Bookmark not defined.] although using FIA with a bigger sample size and higher reagents consumption. The other types of electrodes[Error! Bookmark not defined.] have been used which present, generally speaking, a lower reproducibility[Error! Bookmark not defined.]. In any case, it is clear that the modality corresponding to the combination of differential pulse anodic stripping (DPAS) and flow analysis using the variant proposed allows working with smaller sample volumes. Likewise, better limits of detection than those obtained in batch modalities are achieved, in considerably shorter times, which can be explained in terms of the better contact conditions between the working electrode and the sample. The analysis throughput, in the cases of the lowest concentrations studied, is of 9 samples per hour. In the case of higher concentrations, the frequency can be increased by diminishing the waiting time in each cycle.

Table 3 presents the results obtained by means of procedures similar to the results of the proposed article. The main advantage of our procedure is the drastic reduction of the sample size, without implying a significant decrease in the LOD of the method.

Table 3. Comparison of the LOD obtained by different stationary mercury drop electrode techniques

Technique	Element	Sample size, µL	Accumulation time, seg	LOD, µg L^{-1}	Ref.
DPASV with FIA	Cd	8.000	120	1.5	[28]
DPASV, batch	Cd	10.000	600	700	[29]
MSFIA, screen printed	Cd	1.300	200	0,8	[8]
Mercury drop electrode	Cd	200	480	2.3	This work

Table 4. Analytical procedure for Cd determination using the screen-printed electrode **Error! Bookmark not defined.**

Step	Device	Instruction	Remark
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	Voltagram 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; and PK: pickup; DP: dispense.

2.5.4. Amperometric detection using screen printed

Table 4 summarizes the general analytical procedure for the automated formation of the BiFE and the Cd determination. The analytical performances of the BiF-SPE-MSFIA were evaluated 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 was 1.59%. The linear behaviour 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- Interferences

BiFEs are prone to foul by surface-active compounds that cause deactivation of the electrode surface. The 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 the complexation. Aliquots of seawater were the UV digested to destroy the organic matter and assure that all interferences were due to the inorganic compounds. No differences were found in the Cd measurement in water samples with and without the UV digestion. This reproducibility suggests that both processes: electrode surface fouling and metal complexation were negligible in the analytical conditions.

The Cu^{2+} ions can suppress the peak intensity by intermetallic 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 the UV digestion and 24 hours 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 Cd determination: the linearity and sensitivity of the calibration curve for Cd in acetate buffer were not affected by 100 µg L^{-1} Pb (ip(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, ip = 2.8 ± µA, 3.6% RSD).

4- Conclusion

The comparative study of different flow cell modalities has enabled to:

- The most suitable mercury flow cell for amperometric detections was the D cell of Figure.
- A new procedure for the sequential amperometric detection of Tl(I), Pb(II), and In(III) using the mercury flow cell has been established, which allows to separate the individual signals of the former ions with the aid of on-line NaOH addition.
- A new procedure for carrying out the previous electrolysis in stripping methods has been developed, consisting in the so-called “cyclic stop-wait flow”. This procedure presents several advantages over the other proposed procedures. Such a procedure has been assessed using Cd(II) as the reference element.

- The BiF-SPE-MSFIA is an excellent automatic system for the laboratory or field determination of Cd in the natural samples due to its accuracy, precision, low cost, and low toxicity.

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