Determination of Pb(II) and Cd(II) via anodic stripping voltammetry using an *in-situ* bismuth film electrode. Increasing the sensitivity of the method by the presence of Alizarin Red S

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ABSTRACT

Using the differential pulse anodic stripping voltammetry technique and an *in-situ* bismuth film deposited on a glassy carbon electrode, a simple and sensitive method for rapid Pb(II) and Cd(II) quantification was developed. The effect of the presence of Alizarin Red S (ARS) was studied, and an increase in the sensitivity of the method was obtained. The developed method was compared to another reported method that uses a 0.1 mol L^{-1} acetate buffer medium (pH 4.5). The optimal experimental conditions are listed as follows: [CH$_3$COOH]: 30.0 mmol L^{-1}; [Bi(III)]: 0.75 mg L^{-1}; [ARS]: 40.0 μmol L^{-1}; [Fe(CN)$_6$$^{4-}$]: 50.0 μmol L^{-1}; E$_{dep}$: −1.40 V; t$_{dep}$: 60 s. Under these conditions, the detection limits were 0.16 and 0.09 μg L^{-1} and the linearity was maintained at values as great as 30.0 and 15.0 μg L^{-1} for Pb(II) and Cd(II), respectively. The effect of 35 foreign ions as possible interferents was studied. The method was validated using two certified reference materials (TMDW and TMDA-61.3) with satisfactory results. Finally, the method was applied for the analysis of four natural water samples.

1. Introduction

Heavy metals are considered to be both beneficial and dangerous for human health, depending on concentration. For example, cobalt, iron, zinc, copper, manganese, and other metals are required by living organisms, albeit in low amounts. However, lead, cadmium, mercury, and arsenic are considered to be hazardous, even at lower concentrations [1]. Lead and cadmium are widely dispersed in the environment, and human exposure to either element can cause many adverse health effects due to their toxicity following accumulation in multiple organs in the body. Lead affects the hematopoietic, vascular, renal, peptic, cardiovascular, immunological, reproductive, gastrointestinal, endocrine, and central nervous systems [2]. Cadmium can damage the kidneys, bones, and cardiovascular, hematopoietic, endocrine, and immune systems [3]. Lead and cadmium are associated with the induction of oxidative stress. Cd does not produce radicals by itself but instead replaces copper and iron in cytoplasmic and membrane proteins. Higher concentrations of free Cu and Fe induce oxidative stress by the Fenton reaction. Pb binds to enzymes such as delta-aminolevulinic acid dehydratase and glutathione reductase. This process inhibits enzymatic function, altering different processes and resulting in the generation of reactive oxygen species (ROS) [1,4].

The determination of Pb(II) and Cd(II) in natural and drinking water samples remains a concern, with significant need to monitor the concentrations of these metals to avoid possible chronic intoxication by the consumption of water [5]. The determination of lead and cadmium ions in water samples has been performed using different techniques: UV–vis spectrophotometry, fluorescence methods, ion-selective electrode, electrothermal atomic absorption spectrometry, atomic emission spectroscopy, and inductively coupled plasma mass spectrometry [6]. The electroanalytical techniques offer several advantages: allowing quantification in the field with portable and low cost equipment, simple manipulation, and low cost of maintenance, supplies and accessories. The development of sensors and biosensors for lead and cadmium determination has been a field of relevant study [4]. Biosensors require a fabrication process before measurements can be made. A simpler alternative is the use of adsorptive (AdSV) or anodic stripping voltammetry (ASV). The former method has been applied using different combinations of electrodes and complexing agents, for example, with a hanging mercury drop electrode in the presence of 2-mercaptobenzothiazole [7], gallic acid [8], oxine [9–11], xylenol orange [12], resorcinol [13], clioquinol [14], alizarin [15], 2-hydroxybenzaldehyde benzoylhydrazone [16], and calcon [17]; nafion-ionic liquid-mercury film electrode and morin as a complexing agent [18]; nafion-mercury

film electrodes in the presence of quercetin-5′-sulfonic acid [19], pyrogallol red [20], and, rutin [21] and antimony film electrode with pyrogallol red [22].

The determination of Pb(II) and Cd(II) via anodic stripping voltammetry using an *in-situ* bismuth film electrode (BiFE) has been described in different reports [6,23,34]. According to these reports, the most commonly used supporting electrolyte is a 0.1 mol L^{-1} acetate buffer (pH: 4.5). Previous studies have varied the bismuth concentration from 0.02 to 1.0 mg L^{-1} and applied a deposition potential of -0.95 to -1.60 V in the range from 60 to 300 s. These methods are simple and reproducible, the quantification limits are in the µg L^{-1} level or lower, an unmodified carbon electrode is used to deposit the bismuth film, the cleaning procedure is simple, and the required time for completion is short. Other metallic film electrodes deposited *in-situ* have been reported, such as Sb [35–41], Hg [42–48], and Bi-Sn alloy [49].

Due to the low toxicity of bismuth, research on the development of new methods using BiFE is interesting and should be focused on reducing the time required to analyze samples and increasing the sensitivity of the method.

One alternative to increase the sensitivity of the method can be the addition of a complexing agent. This increases the accumulation of the analyte as a complex by adsorption onto the electrode surface and its subsequent deposition. This behaviour was observed and used for the determination of Se(IV) in the presence of ammonium diethyl dithiophosphate and Cu(II) [50]. A recent work reported the use of 8-hydroxyquinoline for the determination of Pb(II), Cd(II), and Zn(II) with an *in-situ* BiFE [34] by using a combination of anodic and adsorptive stripping voltammetry. The bismuth film and the analytes were reduced and deposited in a first step. Then, the deposited lead, cadmium, and zinc were oxidized by the application of a potential of -0.70 V for 10 s. Due to the presence of the ligand, complexes were formed and adsorbed onto the BiFE surface. The potential scan was performed in the cathodic direction. The analytical response of the three metal ions was increased due to the presence of 8-hydroxyquinoline. In this work, a deposition time of 240 s was applied. A second method was reported using 2-mercaptobenzothiazole as the complexing agent and an *in-situ* BiFE for Pb(II) and Cd(II) determination in tap water was carried out with the use of ASV [6]. The presence of the complexing agent increased the analytical response, although the applied deposition time was 300 s. This long time period reduces the applicability of the method.

Table 1 summarizes the reported electroanalytical methods for Pb(II) and Cd(II) determination using a metal film electrode formed *in-situ*, carbon paste electrodes modified with a metal or metal salt, screen printed electrodes, unmodified electrodes and solid metal electrodes. The use of modified electrodes before metal film formation and *ex-situ* deposits were not included. The aim of this work is to compare our method with other methods that are simple, rapid and do not require the electrode modification before electrochemical deposition. These conditions are essential for the electroanalytical determination of Pb(II) and Cd(II) to increase the applicability of the method in routine analyses. A review of previously reported methods (Table 1) shows that a deposition time of 120 s or greater is required to achieve detection limits on the µg L^{-1} level for Pb(II) and Cd(II). Faster methods (deposition time of 60 s) with detection limits less than the µg L^{-1} level were based on the formation of an *in-situ* mercury film electrode. Today, mercury electrodes are not an alternative for routine analysis. Therefore, the development of new, rapid, simple, sensitive, and environmentally friendly methodologies is required.

To increase the method sensitivity and to reduce the analysis time, the presence of a complexing agent during film formation and analyte deposition could be a promising alternative. The present work reports the development of a method for the determination of Pb(II) and Cd(II) by using anodic stripping voltammetry with an *in-situ* BiFE. The presence of Alizarin Red S (ARS) as a complexing agent and its effect on the sensitivity of the method was studied. A comparison between this

method and the widely used method at pH 4.5 with an *in-situ* BiFE is included.

2. Materials and methods

2.1. Chemicals

A Simplicity water purification system (Millipore Corporation, Bedford, MA, USA) was used to produce deionized water for all associated purposes. Sodium chloride, acetic acid, nitric acid, hydrochloric acid, phosphoric acid, and 30% sodium hydroxide solution were all of suprapur grade. Bi(III), Pb(II), and Cd(II) as nitrate salts and other metal ion solutions were prepared from 1000 mg L^{-1} stock solutions (Merck, Darmstadt, Germany). Potassium hexacyanoferrate(II) trihydrate, potassium fluoride, sodium sulfate, potassium nitrate, ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), 1,2-cyclohexylenedinitrilotetraacetic acid monohydrate (CDTA), perchloric acid, sulfuric acid, and Alizarin Red S monosodium salt were purchased from Merck (Darmstadt, Germany).

A 2.0×10^{-3} mol L^{-1} stock solution of ARS was prepared in deionized water and stored at 4 °C.

TMDA-61.3 (National Research Council Canada, Ottawa, Canada) and CRM-TMDW (High Purity Standards, Charleston, SC, USA) certified reference materials were used for method validation. The certified compositions of each solution are as follows:

TMDA-61.3: Al: 58.4; Sb: 33.5; As: 35.0; Ba: 64.1; Be: 36.8; Bi: 20.4; B: 48.8; Cd: 59.2; Cr: 67.3; Co: 63.6; Cu: 62.0; Fe: 80.0; Pb: 56.0; Li: 34.6; Mn: 76.1; Mo: 730; Ni: 56.7; Rb: 3.20; Se: 40.4; Sr: 114; Tl: 37.2; Sn: 56.0; Ti: 37.0; U: 36.2; V: 70.2 and Zn: 72.6 µg L^{-1}.

CRM-TMDW: Al: 120; Sb: 10.0; Ba: 50.0; As: 80.0; Be: 20.0; Bi: 10.0; Cd: 10.0; Ca: 35000; Cr: 20.0; Co: 25.0; Cu: 20.0; Fe: 100.0; Pb: 40.0; Li: 20.0; Mg: 9000; Mn: 40.0; Mo: 100; Ni: 60.0; K: 2500; Rb: 10.0; Se: 10.0; Na: 6000; Sr: 250; Tl: 10.0; U: 10.0; V: 30.0 and Zn: 70.0 µg L^{-1}.

2.2. Apparatus

Voltammetric measurements were obtained on a CHI6088E Electrochemical Analyzer. A 3.0 mm glassy carbon electrode was used for *in-situ* bismuth film deposition (working electrode), the reference electrode was an Ag/AgCl/KCl (3.0 mol L^{-1}), and the auxiliary electrode was a platinum wire (CH Instruments, Austin, TX, USA). A 15 mL glass cell with a Teflon cell top and a 4 mm Teflon rod placed in an RDE-2 Rotating Disk Electrode Cell Stand (Basi Corporate Headquarters, West Lafayette, IN, USA) were used for electrochemical measurements and stirring.

The pH was measured with an Orion model 430 pH meter (Cole-Parmer, Vernon Hills, IL, USA).

Spectrophotometric measurements were obtained with an HP 8453 diode-array spectrophotometer (Hewlett-Packard, Wilmington, DE, USA).

Field-emission scanning electron microscopy (FESEM) micrographs were obtained using an FEI QUANTA FEG 250 microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA). The micrographs were recorded under an accelerating voltage of 20 kV.

2.3. Preparation of the in-situ BiFE and voltammetric measurements.

The glassy carbon electrode was polished on a microcloth pad with 0.3 µm alumina for 30 s. Then, the electrode was rinsed with deionized water and polished with 0.05 µm alumina until a mirror shine of the electrode surface. The electrode was rinsed with an abundance of deionized water and sonicated in water for 30 s. After each polishing process, in a 1.0 mol L^{-1} H$_2$SO$_4$ solution, a potential of 0.80 V was applied for 30 s, and then -1.50 V for 30 s under stirring. Later, the electrode was stabilized measuring 10 segments by cyclic voltammetry between 1.00 and -1.00 V using a scan rate of 100 mV s^{-1}.

Table 1

Electroanalytical methods for Pb(II) and Cd(II) determination using a solid metal, unmodified, screen printed, and *in-situ* metal film electrodes and anodic stripping voltammetry.

Electrode	Modifier in solution	Technique	Supporting Electrolyte	Sample	Linear range (μg L^{-1})	Detection limit (μg L^{-1})	Deposition time (s)	Ref.
AgRDE	—	SWSASV	HNO$_3$ 0.01 M NaCl 0.01 M	Drinking water	0.08–62.2 0.6–28.1	0.001 0.1	90	[51]
RSRE	—	DPASV	KCl 0.01 M HNO$_3$ 0.01 M	River water Tap water	NR-8.3 NR-9.0	0.1 0.3	120	[52]
EPPGE	—	LSASV	ABS 0.1 M pH: 4.6	—	2–200 2–200	0.2 0.3	240	[53]
304SSE	—	SWASV	ABS 0.1 M (pH: 4.5)	Ground water	15.5–1036 56.2–562.1	6.8 25.9	300	[54]
CFSbFME	—	SWASV	HCl 0.01 M	—	20–100 20–100	3.1 1.9	120	[35]
BDDSbFE	—	LSASV	HCl 0.1 M	—	50–500 50–500	25.7 38.1	120	[36]
SbFE	—	SWASV	HCl 0.01 M	Phosphorite Lake water	NR-120 NR-120	0.95 1.3	240	[37]
SbSPCE-CNF	—	DPASV	HCl 0.01 M KNO$_3$ 0.01 M	—	6.9–100.9 3.7–100.3	2.1 1.1	120	[38]
SbSPCE	—	DPASV	ABS 0.01 M (pH: 4.5) KNO$_3$ 0.01 M	—	16.8–62.6 11.5–72.4	5.0 3.4	120	[39]
SbFE	—	SIA-SWASV	HCl 0.5 M	s-Tap water	4.0–120.0 5.0–100.0	1.2 1.4	120	[40]
CPSbFE	—	SWASV	HCl 0.01 M	s-Lake water	5–50 5–50	0.2 0.8	120	[41]
SPE-HgAc	—	SWASV	NaCl 0.6 M (pH: 8)	s-Seawater	10–2000 10–2000	1.8 2.9	120	[55]
CGFHgFME	—	SWASV	ABS 0.84 mM (pH: 3.7)	—	NR-17.8 NR-9.7	0.1 0.06	120	[42]
HgFE	—	LSASV	ABS 0.18 M (pH: 5.5) NaCl 0.1 M	Blood	—	0.04 0.02	900	[43]
HgFE	—	DPASV	pH 2.9	Antarctic snow	—	0.001 0.0005	600	[44]
HgFE	—	ASV	HCl 0.5 M	Wines	—	—	120	[45]
BDDHgFE	—	DPASV	ABS 0.1 M (pH: 5.2)	—	5–1000 1–1000	1.0 5.0	210	[46]
HgFE	—	DPASV	HCl 0.05 M KNO3 0.1 M	Tap water Spring water River water	0.15–60 0.3–50	0.08 0.25	60	[47]
HgFE	Fe^{3+}	Magneto SWASV	HNO$_3$ 0.03 M KNO$_3$ 0.1 M	Wastewater	2.1–207.2 1.1–112.4	0.18 0.10	60	[48]
BiSnFE	—	SWASV	ABS 0.1 M (pH: 4.5)	Tap water	2.2–390 2.0–50	1.0 1.0	60	[49]
BiBE	—	SWASV	ABS 0.1 M (pH: 5.0)	River water	10–100 10–100	0.09 0.05	180	[56]
BiOClCPE	—	SWASV	NaCl 0.1 M (pH: 3.0)	Soil	10–400 10–450	0.42 0.76	300	[57]
BiCPE	—	SWASV	ABS 0.2 M (pH: 4.5)	s-Tap water	NR-100 NRv100	0.9 1.2	300	[58]
BiOSPE	—	SWASV	ABS 0.1 M (pH: 4.5)	River water	20–100 20–100	2.3 1.5	300	[59]
BiFE	—	SWASV	ABS 0.1 M (pH: 4.5)	River water	5–110 5–110	1.11 1.29	120	[23]
BiFE	—	DPASV	ABS 0.1 M (pH: 4.5)	—	38.2–233 36.8–233	11.5 11.0	240	[24]
BiFE	—	SWASV	ABS 0.1 M (pH: 4.5)	Rice	5–200 10–200	0.06 0.11	300	[25]
BiCTE	—	SWASV	ABS 0.1 M (pH: 4.6)	River water	5–110 5–110	0.87 1.08	300	[26]
CPBiFE	—	SWASV	ABS 0.1–1.0 M (pH: 4.5)	—	NR	0.1 0.15	120	[27]
BiFE	—	SWASV	HCl 0.5 M	Noodles soup	20–1000 20–1000	7.0 4.0	240	[28]
EPPGBiFE	—	SWASV	ABS 0.1 M (pH: 4.5)	s-River water	0.1–20 0.1–10	0.08 0.06	240	[29]
BiFEv	—	SWASV	ABS 0.1 M (pH: 4.5)	—	40–200 40–200	1.1 —	120	[30]
BiFµE	—	LSASV	ABS (pH: 4.5)	Drinking water Wine and tomato sauce	10.4–207.2 5.6–112-	0.6 0.9	60	[31]
SPCBiFE	—	SWASV	ABS 0.1 M (pH: 4.5)	Tap water	10–100 10–100	2.5 3.6	120	[32]

Table 1 (*continued*)

Electrode	Modifier in solution	Technique	Supporting Electrolyte	Sample	Linear range (µg L^{-1})	Detection limit (µg L^{-1})	Deposition time (s)	Ref.
BiFE	—	SWASV	ABS 0.1 M (pH: 4.5)	s-Tap water	30–90	30	120	[33]
				s-Soil sample	30–90	30		
BiFE	8-hydroxyquinoline	SWAAdSV	HEPES 0.01 M (pH: 6.5)	Lake water	2–110	0.45	240	[34]
				River water	2–110	0.17		
BiFE	Mesoporous silica 2-mercaptobenzothiazole	SWASV	ABS 0.1 M (pH: 6.0)	Tap water	5–50	0.80	300	[6]
					5–50	0.56		
BiFE	Alizarin red S	DPASV	Acetic acid 0.03 M	Tap water	0.48–0.27-	0.16	60	This work
				River water		0.09		

304SSE: 304 stainless steel electrode; **ABS:** Acetate buffer solution; **AgRDE:** Silver rotating disk electrode; **BDDHgFE:** Boron doped diamond electrode modified with a mercury film; **BDDSbFE:** Boron doped diamond electrode modified with a bismuth film; **BiBE:** Bismuth bulk electrode; **BiCPE:** Bismuth powder carbon paste electrode; **BiCTE:** Bismuth carbon thread electrode; **BiFE:** Bismuth film electode; **BiFµE:** Bismuth film microelectrode; **BiOClCPE:** Bismuth oxychloride carbon paste electrode; **BiOSPE:** Bismuth oxide screen printed electrode; **BiSnFE:** Bismuth-tin film electrode; **CFSbFME:** Carbon fiber antimony film microelectrode; **CGFHgFME:** Cilindrical graphite fiber mercury film microelectrode; **CPBiFE:** Carbon paste bismuth film electrode; **CPSbFE:** Carbon paste antimony film electrode; **DPASV:** Differential pulse anodic stripping voltammetry; **EPPGE:** Edge plane pyrolytic graphite electrode; **EPPGBiFE:** Edge plane pyrolytic bismuth film electrode; **HgFE:** Mercury film electrode; **LSASV:** Linear scan anodic stripping voltammetry; **M:** mol L^{-1}; **RSRE:** Renovated silver ring electrode; **s-:** spiked; **SbFCPE:** Antimony film carbon paste electrode; **SbFE:** Antimony film electrode; **SbSPCE:** Antimony film screen printed carbon electrode; **SbSPCE-CNF:** Screen printed carbon nanofiber antimony film electrode; **SIA:** Sequential inject analysis; **SPCBiFE:** Screen printed carbon bismuth film electrode; **SPE-HgAc:** Screen printed graphite electrode modified with plasticizer and mercury acetate; **SWAAdSV:** Square wave anodic adsorptive stripping voltammetry; **SWASV:** Square wave anodic stripping voltammetry; **SWSASV:** Square wave subtractive anodic stripping voltammetry.

Bismuth film deposition and analyte preconcentration were performed simultaneously. Acetic acid (150.0 µL of 2.0 mol L^{-1}), 150.0 µL of 50.0 mg L^{-1} Bi(III) stock solution, and 200.0 µL of 2.0 mmol L^{-1} ARS aqueous solution were added to the voltammetric cell. A final volume of 10.0 mL was filled with deionized water. A potential of −1.40 V was applied for 60 s under stirring (5000 rpm). The stirring of the solution was stopped. After 10 s, the potential scan was performed using differential pulse voltammetry from −1.20 to 0.50 V (increment potential: 4 mV; amplitude: 50 mV; pulse width: 25 ms; sampling width: 17 ms; pulse period: 50 ms). A cleaning step was performed before each measurement. For 20 s, a potential of 0.75 V was applied to remove the bismuth film and other deposited species. Aliquots of 0.2 or 1.0 mg L^{-1} Pb(II) and Cd(II) solutions were added into the electrochemical cell for the construction of the calibration plots. All measurements were performed at 25 °C and in triplicate.

2.4. Voltammetric measurement procedure for the validation of the method and the sample analyses

Different volumes of certified reference materials, water, and spiked water samples were pipetted into the voltammetric cell (1.0 mL of TMDW, 500 µL of TMDA-61.3, and 9.68 mL of real samples). If needed, the pH was adjusted to neutrality with 1.0 mol L^{-1} NaOH or HNO$_3$. Aliquots of acetic acid, Bi(III) and Alizarin Red S solutions were added to the electrochemical cell (Section 2.3) and 5.0 µL of 1.0×10^{-1} mol L^{-1} K$_4$Fe(CN)$_6$. A final volume of 10.0 mL was filled with deionized water. Three voltammograms were recorded. Then, aliquots of 0.2 or 1.0 µg L^{-1} Pb(II) and Cd(II) stock solutions were added into the electrochemical cell, the voltammograms were recorded and the calibration plots were constructed. The measurements were performed using the procedure reported in Section 2.3. The standard addition method was used for validation and sample analysis. The analyzed real samples were creek water from the city of Talca, two river water samples from the Mapocho river and the San Francisco river (city of Santiago) and tap water from the city of Quintero. In a second stage, these samples were spiked with a Pb(II) and Cd(II) standard solution and were analyzed to confirm the obtained results.

2.5. Baseline subtraction of the voltammetric signals

Baseline subtraction of the oxidation signals of Pb(II) and Cd(II) was performed using the Savitzky-Golay algorithm (polynomial order: 2) and the peak area of each processed signal was determined.

3. Results and discussion

From previous reports, the most widely used supporting electrolyte for the determination of Pb(II) and Cd(II) using an *in-situ* BiFE has been a 0.1 mol L^{-1} acetate buffer solution (pH 4.5). In preliminary studies, the effect of the presence of ARS was evaluated in this medium. The addition of ARS to a Pb(II) and Cd(II) solution caused a loss of the Pb and Cd signal resolution. In addition, the oxidation signal of ARS overlapped the oxidation signal of lead. This behavior was slightly observed under acidic conditions. Therefore, a study of the effect of different acids and their concentrations on the analytical responses of Pb and Cd was performed in the presence of ARS.

3.1. Supporting electrolyte composition

The presence of nitric, sulfuric, perchloric, phosphoric, hydrochloric, and acetic acid was studied as the supporting electrolyte at different concentrations of each. The lowest intensities of the oxidation signals of Pb and Cd were obtained in the presence of nitric, sulfuric, and hydrochloric acids. The highest responses for both metals were achieved in an acetic acid medium. Fig. S1 shows the effect of the different acids and their concentrations over the peak area of the Pb and Cd oxidation signals. The effect of the acetic acid concentration was studied at two concentrations of Pb(II) and Cd(II), 1.0 and 10.0 µg L^{-1} (Fig. S2A). A concentration of 30.0 mmol L^{-1} was chosen as the optimal concentration, an intermediate value between the concentration of the highest Pb and Cd signals at 1.0 and 10.0 µg L^{-1}. As mentioned above, the most widely used medium for Pb(II) and Cd(II) analysis with ASV using a BiFE is an acetate buffer solution at pH 4.5. Therefore, from an initial acetic acid solution (30.0 mmol L^{-1}), the pH was increased by the addition of aliquots of 1.0 mol L^{-1} NaOH, and the peak areas of the oxidation signals of Pb and Cd were measured (Fig. S2B). As the pH was increased, the peak area of both metal signals decreased. In further experiments, a 30.0 mmol L^{-1} acetic acid solution was used.

3.2. The effects of the Bi(III) and ARS concentrations

The effects of the Bi(III) and ARS concentrations were studied using a deposition potential of −1.20 V and a deposition time of 60 s for the *in-situ* BiFE formation. The Bi(III) concentration was studied in the range from 0.0 to 2.15 mg L^{-1} (Fig. 1A). The maximum responses were found at a Bi(III) concentration of 0.75 mg L^{-1} for Pb(II) and Cd(II) at 1.0 and 10.0 µg L^{-1}, such that this Bi(III) concentration was chosen as optimal.
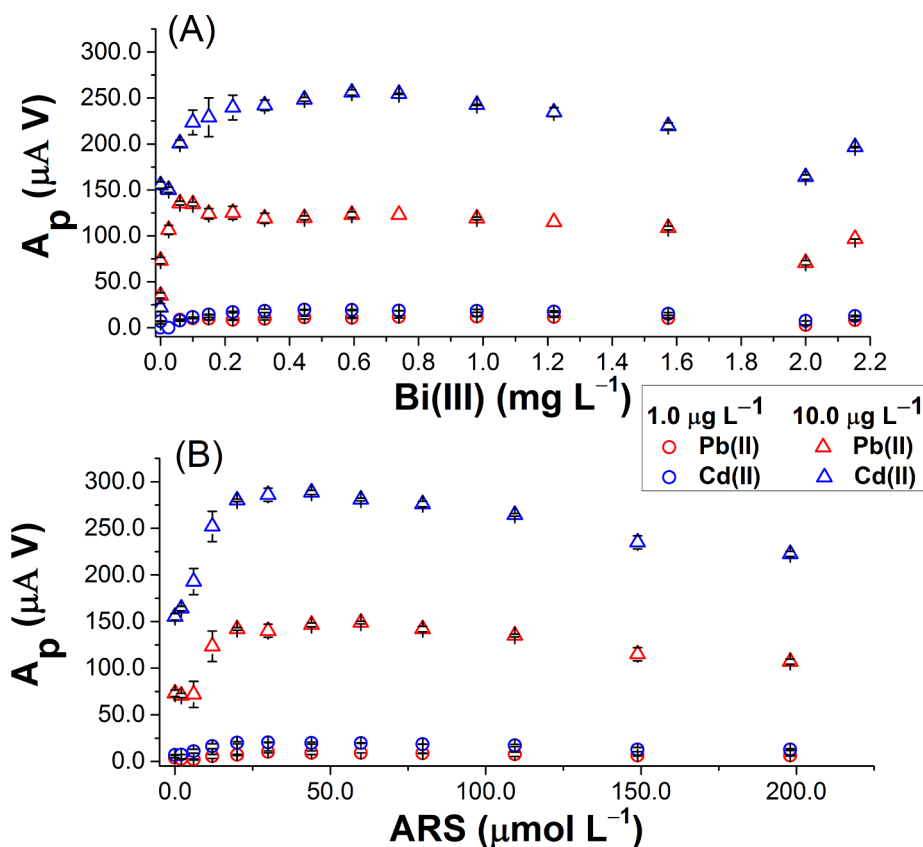
Fig. 1. Effect of the Bi(III) (A) and ARS (B) concentration on the analytical response of Pb and Cd. Conditions: [CH$_3$COOH]: 30.0 mmol L^{-1}; [Pb(II)] and [Cd(II)]: 1.0 and 10.0 µg L^{-1}; E$_{dep}$: −1.20 V; t$_{dep}$: 60 s. (A) [ARS]: 20.0 µmol L^{-1}; (B) [Bi(III)]: 0.75 mg L^{-1}.

Fig. 1B shows the effect of the ARS concentration on the peak area of Pb and Cd oxidation signals (1.0 and 10.0 µg L^{-1}). The analytical response of both metals increased due to the addition of ARS, until a ligand concentration of 40.0 µmol L^{-1}. This ARS concentration was used in further studies and its effect over the sensitivity and the linear range of the method was evaluated (Section 3.5).

3.3. The effects of the deposition potential and time

The influence of the deposition potential on the oxidation signals of Pb and Cd was studied in the range from −0.40 to −2.00 V. Fig. 2A shows the effect of the deposition potential on the peak areas of the Pb and Cd oxidation signals. The analytical response of both metals increased as the applied deposition potential grew increasingly negative. A sharp increment was observed between −0.40 and −0.60 V for lead due to its oxidation peak potential, which was −0.57 V. Therefore, the application of a deposition potential that was more negative than −0.60 V allowed the reduction of Pb(II) in the solution while depositing it on the BiFE surface. The same behaviour was observed for Cd between the deposition potentials of −0.80 and −1.00 V, where the oxidation peak potential of Cd was −0.85 V. Although the highest analytical responses were obtained at −2.00 V, nonetheless a deposition potential of −1.40 V was chosen as optimal. In real samples, the application of a deposition potential more negative than −1.40 V generated broader signals, with a loss of signal resolution.

Fig. 2B shows the effect of the deposition time on the analytical response of both metals. This effect was studied in the range from 0 to 300 s. A linear increase of the peak areas of the oxidation signals of Pb and Cd was observed until a deposition time of 60 s. The application of longer deposition times generated an increase of the analytical response with a lower ratio between the signal area and the deposition time. A deposition time of 60 s was used in subsequent experiments. However,

the application of a longer deposition time could be used to increase the sensitivity of the method. In the analysis of real samples, longer deposition times could be required if the Pb(II) and Cd(II) concentrations are low.

3.4. Investigation of interfering phenomena

The effect of different anions, masking agents, metal ions, and other inorganic species was investigated over the analytical response of lead and cadmium at 5.0 µg L^{-1} of Pb(II) and Cd(II) under optimal conditions. Fig. S3 shows the effects of nitrate, chloride, fluoride, bromide, and sulfate anion concentration over the peak areas of the oxidation signals of Pb and Cd. Lead and cadmium signals tended to decrease due to the increase of the concentration of these anions. From a concentration of 25.0 and 250.0 µmol L^{-1} of each anion, the depletion of the Pb and Cd signals, respectively, was sharper. A decrease by approximately 80% was found for both metals in the presence of 0.1 mol L^{-1} of each anion.

CDTA and EDTA were evaluated as masking agents to prevent the possible interference of other ions. However, the addition of EDTA and CDTA into the solution containing Pb(II) and Cd(II) generated an abrupt decrease of the Pb and Cd oxidation signals (Fig. S4). Therefore, the use of these complexing agents as masking agents was discarded. Cu(II) has been reported as one of the most important interferents for Pb(II) and Cd(II) determination using an in-situ BiFE via ASV [26,34]. Hexacyanoferrate(II) [60] has been used as a masking agent to decrease the interference of Cu(II). The effect of Fe(CN)$_6^{4-}$ on the Pb and Cd oxidation signals was studied (Fig. S4). If Fe(CN)$_6^{4-}$ was not used as a masking agent, then Cu(II) interfered at any concentration, depleting both the Pb and Cd signals. Therefore, a concentration of 50.0 µmol L^{-1} of hexacyanoferrate (II) was chosen as optimal and as a component of the supporting electrolyte.
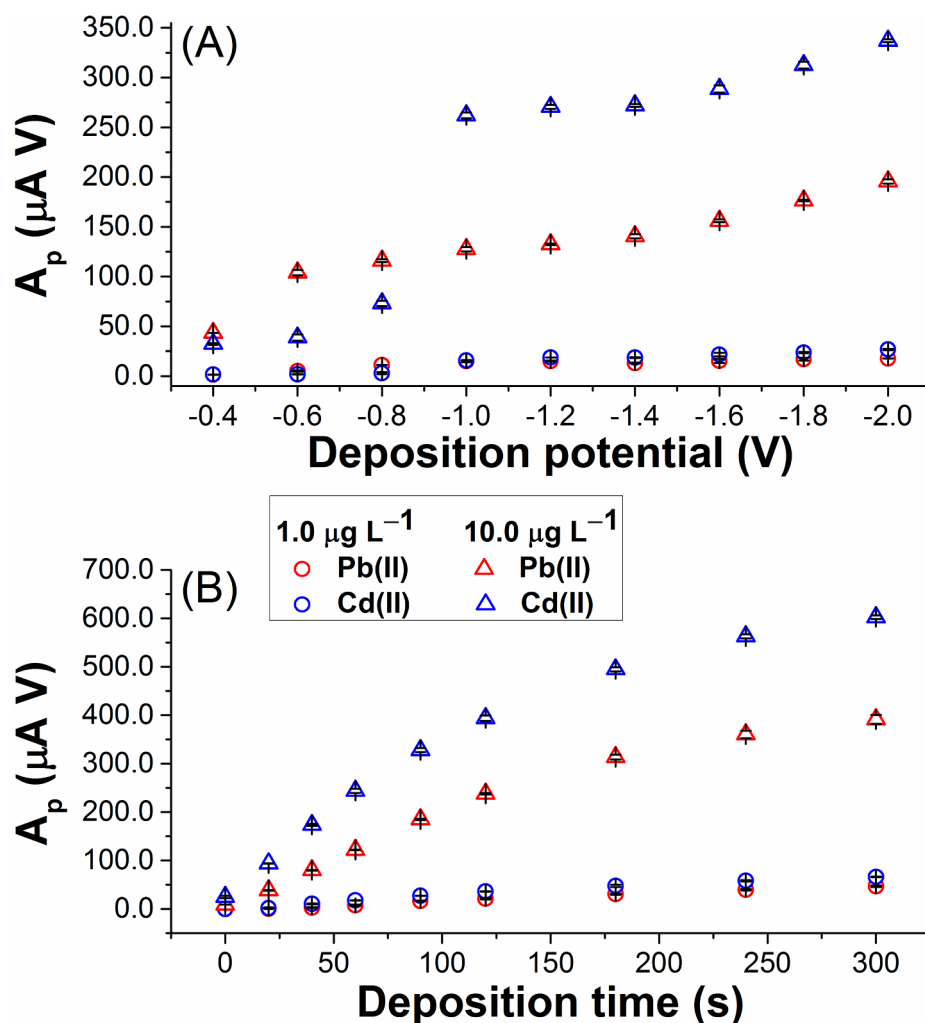
Fig. 2. Effect of the deposition potential (A) and deposition time (B) on the peak area of the oxidation signal of Pb and Cd. Conditions: [CH$_3$COOH]: 30.0 mmol L^{-1}; [Bi(III)]: 0.75 mg L^{-1}; [ARS]: 40.0 μmol L^{-1}; [Pb(II)] and [Cd(II)]: 1.0 and 10.0 μg L^{-1}. (A) t$_{dep}$: 60 s; (B) E$_{dep}$: −1.40 V.

The effect of possible interfering species on the analytical responses of Pb and Cd was studied in the presence of Fe(CN)$_6^{4-}$ (50.0 μmol L^{-1}). The interferent:Pb/Cd ratio that did not generate a variation of the peak area of the signal greater than a ± 10% was determined. In addition, the percentage peak area variation in a 100-fold excess of each interferent was determined. The most relevant interferents, which generated peak signal variations greater than ± 10% at 5-fold excess or less were Al(III), Se(IV), Hg(II), Ni(II), and W(VI) for lead determination, and Al(III), Co(II), Tl(I), Hg(II), Ni(II), Sc(III), Se(IV), Cu(II), Sn(IV), Zr(IV), Ti(IV), Mo(VI), W(VI), and Pb(II) for cadmium determination. Only Tl(I) interfered with Cd(II) determination by overlapping its oxidation signal. The overlap generates a change in the cadmium signal symmetry, which allows for the interference to be detected in real sample analysis if Tl(I) is present at a sufficiently high concentration to interfere. The other ions caused a peak signal decrease, interfering by depleting of the sensitivity of the method. In the present work, an exhaustive evaluation of the effect of foreign ions on the analytical responses of Pb(II) and Cd(II) was made. The study of interference in previous reports has not been extensive, and the effect of many ions has not been evaluated. The effect of the most relevant foreign ions mentioned before was studied at the most widely supporting electrolyte conditions (0.1 mol L^{-1} acetate buffer solution, pH 4.5). Table 2 summarizes the results of the interference study.

3.5. Analytical performance

Calibration plots in the absence and in the presence of ARS were constructed under optimal conditions (30.0 mmol L^{-1} acetic acid, 0.75 mg L^{-1} Bi(III), 40.0 μmol L^{-1} ARS, 50.0 μmol L^{-1} Fe(CN)$_6^{2-}$, E$_{dep}$: −1.40 V, and t$_{dep}$: 60 s) and using a 0.1 mol L^{-1} acetate buffer solution at pH 4.5. The measurements were performed using the same deposition conditions (E$_{dep}$ and t$_{dep}$) and, bismuth and hexacyanoferrate(II) concentrations. From the linear regressions of the calibration plots (Table 3), it was observed that the sensitivity (slope of calibration plot) of the method in the presence of ARS was greater than the sensitivity in the absence of ARS using acetic acid (30.0 mmol L^{-1}) as the supporting electrolyte at factors of 1.41 and 1.09 for lead and cadmium, respectively. If the sensitivity in the presence of ARS and using 0.1 mol L^{-1} acetate buffer is compared, the sensitivity was increased by factors of 2.54 and 1.78 for lead and cadmium, respectively. The addition of ARS caused an increase of the sensitivity, but the linear range of the method was shorter than in the absence of the ARS. Fig. 3 shows the voltammograms and the calibration plot (inset) obtained in the presence of 40.0 μmol L^{-1} of ARS in a 30.0 mmol L^{-1} acetic acid medium.

The proposed method in which 60 and 180 s deposition times were applied was also evaluated. A proportional increase of the sensitivities for both analytes was found based on the application of a longer deposition time. The linearity of the method using a deposition time of

Table 2

Tolerance of foreign ions that do not produce a signal variation higher than $\pm$ 10% and percentage variation of the Pb(II) and Cd(II) signals in the presence of a 100-fold excess of foreign metals ions. Pb(II) and Cd(II) concentration: 5.0 µg L^{-1}.

Int	[Int]:[Pb (II)] Ratio	% ΔI_p [Int]:[Pb (II)] 100:1	Int	[Int]:[Cd (II)] Ratio	% ΔI_p [Int]:[Cd (II)] 100:1
Al(III)	< 1 (100)	− 36	Al(III)	< 1 (< 1)	− 50
Se(IV)	1 (5)	− 100	Co(II)	< 1 (1)	+ 137
Hg(II)	2.5 (10)	− 32	Tl(I)	1 (< 1)	+ 1200
Ni(II)	5 (2.5)	− 100	Hg(II)	1 (10)	− 25
W(VI)	5 (5)	− 23	Ni(II)	1 (1)	− 100
Mo(VI)	10 (10)	+ 1700	Sc(III)	2.5 (100)	− 48
Co(II)	10 (2.5)	− 46	Se(IV)	2.5 (2.5)	− 100
Sn(IV)	10 (10)	+ 60	Cu(II)	5 (1)	− 88
Zr(IV)	10 (100)	− 35	Sn(IV)	5 (50)	− 26
V(V)	10	+ 70	Zr(IV)	5 (1)	− 55
Fe(III)	10	− 100	Ti(IV)	5 (75)	− 15
Cu(II)	25 (10)	− 25	Mo(VI)	5 (5)	− 43
Sc(III)	25 (100)	− 30	W(VI)	5 (10)	− 18
Sb(III)	25	− 36	Pb(II)	5	+ 15
Ru(III)	25	− 22	Fe(III)	10	− 100
Tl(I)	50 (2.5)	− 17	Ga(III)	10	+ 41
Ge(IV)	75	+ 14	V(V)	10	− 20
Cr(III)	75	− 15	Sb(III)	10	− 40
Cd(II)	75	− 11	Zn(II)	25	− 30
Ag(I)	100	− 5	Ru(III)	25	− 62
Ga(III)	100	+ 5	Ag(I)	25	− 20
Zn(II)	100	+ 9	Ge(IV)	100	+ 2
Ti(IV)	100 (75)	+ 7	Cr(III)	100	− 9
As(V)	100	− 9	As(V)	100	− 6
U(VI)	100	− 8	U(VI)	100	− 7
Mn(II)	100	− 8	Mn(II)	100	− 7
Te(IV)v	100	− 5	Te(IV)	100	− 5
As(III)	100	− 7	As(III)	100	− 9
Ca(II)	100	− 5	Ca(II)	100	− 7
Be(II)	100	+ 1	Be(II)	100	− 7
Ba(II)	100	− 3	Ba(II)	100	− 8
Mg(II)	100	+ 1	Mg(II)	100	− 6
Cs(I)	100	− 6	Cs(I)	100	− 9
Li(I)	100	− 7	Li(I)	100	− 8
K(I)	100	− 6	K(I)	100	− 7
Na(I)	100	− 8	Na(I)	100	− 9

(): Maximal ratio of foreign ions that generate a peak signal variation of Pb(II) and Cd(II) (5.0 µg L^{-1}) higher than $\pm$ 10% using an acetate buffer solution (0.1 mol L^{-1}, pH 4.5) as supporting electrolyte. Int: Interferent.

60 s was maintained until 30.0 and 15.0 µg L^{-1} for Pb(II) and Cd(II), respectively. Applying a deposition time of 180 s, the linearity was maintained until 8.0 µg L^{-1} for both metal ions.

The calculated detection limits (3.3 σ) were 0.16 and 0.09 µg L^{-1} when applying a deposition time of 60 s for lead and cadmium, respectively. For a deposition time of 180 s, the detection limits were 0.03 µg L^{-1} for both metal ions. The quantification limits (10 σ) were 0.48 and 0.27 µg L^{-1} (t$_{dep}$: 60 s) for lead and cadmium, respectively. Using a deposition time of 180 s, the quantification limits for lead and cadmium were 0.09 and 0.08 µg L^{-1}, respectively. The upper limit of the linear range of Pb(II) was two times larger than Cd(II) (t$_{dep}$: 60 s). This difference is related to the higher sensitivity achieved for Cd(II)

determination. If the linear ranges are presented as a multiple of the quantification limits (QLs), linearity was maintained until 62.5 and 55.6 QL for Pb(II) and Cd(II), respectively. Therefore, both linear ranges are very similar.

The repeatability of the method was 3.2% and 3.1% for Pb(II) and Cd(II), respectively. Repeatability was determined by measuring a 5.0 µg L^{-1} solution of Pb(II) and Cd(II) twenty times under optimal conditions and using a deposition time of 60 s. The reproducibility was evaluated by performing ten assays in which the concentration of Pb(II) and Cd(II) was 5.0 µg L^{-1} and where a deposition time of 60 s was applied under optimized conditions. For each assay, the glassy carbon electrode was polished and a fresh solution was used. The reproducibility was 8.2 and 8.6% for Pb(II) and Cd(II), respectively.

Using the detection limit as a comparison parameter, the present method achieves the detection of Pb(II) and Cd(II) (t$_{dep}$: 60 s) at lower concentrations than in previous reports that used BiFE. Similar detection limits were reported in some studies [6,25,27,29,31,34] as is shown in Table 1. However, the deposition times applied were at least twice as long. The achieved detection limits are comparable to the detection limits reported using a HgFE with the same deposition time (60 s) [47,48]. Therefore, the present method allows the substitution of mercury, while retaining the good performance of that electrode.

The developed method was affected by different ions, as reported in other methods: Cu(II) [6,32,34], Co(II) [6,23], and Ni(II) [23,24]. However, the study of interfering phenomena presented in this work includes many ions that have not been considered in previous reports.

3.6. Validation of the method and real sample analysis

The method was validated using two different certified reference materials (TMDW and TMDA-61.3). The matrix composition, the analytes, and the concentrations of the other ions were different in the certified reference materials. Aliquots of the certified reference materials were analyzed using a deposition of 60 s. The concentrations of Pb(II) and Cd(II) in the electrochemical cell for the analysis of TMDW were 4.0 and 1.0 µg L^{-1}, respectively. The concentration determined for Pb(II) was 4.13 $\pm$ 0.60 µg L^{-1} (RE: 3.3%) and for Cd(II), was 1.08 $\pm$ 0.05 µg L^{-1} (RE: 8.0%), whereas the concentrations of Pb(II) and Cd(II) in the electrochemical cell for the analysis of TMDA-61.3 were 2.3 and 2.9 µg L^{-1}, respectively. The concentration determined for Pb(II) was 2.45 $\pm$ 0.07 µg L^{-1} (RE: 6.5%) and for Cd(II), was 2.7 $\pm$ 0.05 µg L^{-1} (RE: 6.9%). Satisfactory results were obtained, considering the low concentration of Pb(II) and Cd(II) in the electrochemical cell and the presence of other ions (Cu, Tl, Mo, Al, Co, Ni, and Se).

The developed method was used to analyze four water samples. A deposition time of 120 s was used due to the low concentration of the analytes in the samples. Pb(II) was detected in two samples and Cd(II) in one. The samples were spiked with 0.30 µg L^{-1} of Pb(II) and Cd(II). Successfully, the results agreed between the concentration of the analytes determined in the samples and the spiked samples. The results of the analysis of the real samples are summarized in Table 4.

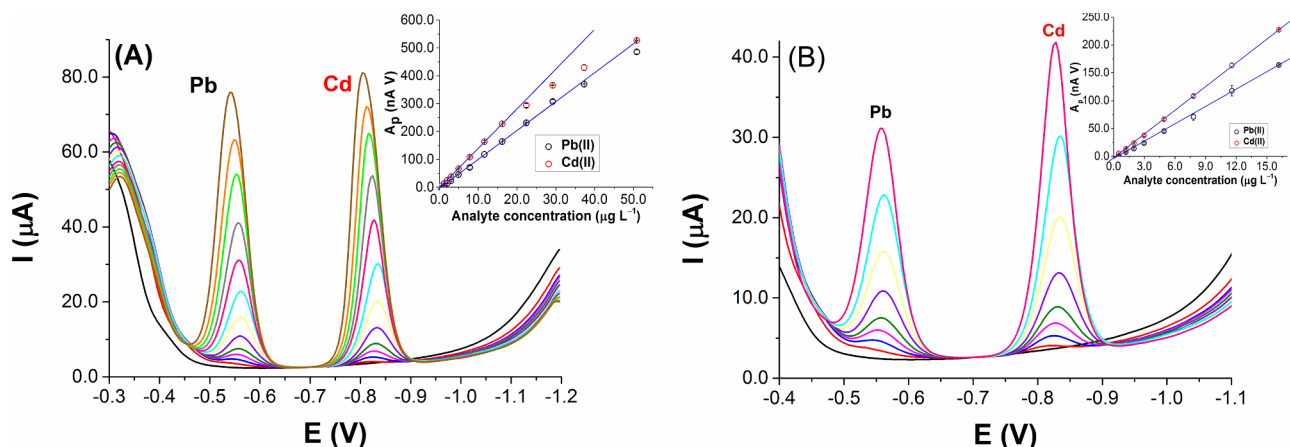From the presented results, some advantages of the method

Table 3

Comparison of the analytical performance of the method in the absence and the presence of ARS and using an acetate buffer solution as supporting electrolyte.

Supporting electrolyte	C$_{ARS}$ (µmol L^{-1})	t$_{dep}$ (s)	Analyte	Slope (nA V L µg^{-1})	Intercept (nA V)	R^2	Linearity up to (µg L^{-1})
Acetic acid 30.0 mmol L^{-1}	0.0	60	Pb	7.36	− 3.86	0.9994	30.0
			Cd	12.97	− 5.46	0.9994	25.0
Acetic acid 30.0 mmol L^{-1}	40.0	60	Pb	10.37	− 3.49	0.9997	30.0
			Cd	14.16	− 1.63	0.9999	15.0
Acetate buffer 0.1 mol L^{-1}; pH 4.5	0.0	60	Pb	4.09	− 7.51	0.9972	50.0
			Cd	7.96	− 1.52	0.9999	50.0
Acetic acid 30.0 mmol L^{-1}	40.0	180	Pb	33.82	0.32	0.9996	8.0
			Cd	41.31	0.39	0.9998	8.0

Fig. 3. Voltammograms and calibration plot (inset) under optimal conditions. Conditions: $[CH_3COOH]$: 30.0 mmol L^{-1}; $[Bi(III)]$: 0.75 mg L^{-1}; $[ARS]$: 40.0 µmol L^{-1}; $[Fe(CN)_6^{4-}]$: 50.0 µmol L^{-1}; E_{dep}: −1.40 V; t_{dep}: 60 s. (A) $[Pb(II)]$ and $[Cd(II)]$: 0.5–50.0 µg L^{-1}. (B) $[Pb(II)]$ and $[Cd(II)]$: 0.5–16.0 µg L^{-1}. (■) blank; (—) 0.5; (—) 1.2; (—) 2.0; (—) 3.0; (—) 4.9; (—) 7.8; (—) 11.6; (—) 16.0 µg L^{-1} of Pb(II) and Cd(II).

Table 4
Analysis of real and real spiked samples.

Sample	Concentration added of the analytes (µg L^{-1})	Determined Pb(II) concentration (SD) (µg L^{-1})	Determined Cd(II) concentration (SD) (µg L^{-1})
CW	0.0	0.21 (0.07)	ND
	0.30	0.52 (0.08)	0.27 (0.01)
MRW	0.0	ND	ND
	0.30	0.28 (0.01)	0.29 (0.02)
SFRW	0.0	ND	0.55 (0.03)
	0.30	0.31 (0.03)	0.88 (0.05)
TW	0.0	1.86 (0.10)	ND
	0.30	2.23 (0.06)	0.34 (0.02)

CW: Creek water; MRW: Mapocho river water; ND: Not detected; SFRW: San Francisco river water; SD: Standard deviation; TW: Tap water.

presented here can be highlighted in comparison to the methods presented in previous reports. The sensitivity of the method is high, achieving lower detection and quantification limits when applying a short deposition time (60 s). This is relevant for reduction in analysis time and increasing the applicability of the method in routine analysis. The results are similar to or better than those of reported methods that use a mercury film electrode. The effect of 35 foreign ions was studied. An exhaustive evaluation of possible interferences has not been reported for the determination of Pb(II) and Cd(II) until now. The accuracy of the method was demonstrated by the analysis of two certified reference materials with satisfactory results. Moreover, the feasible application of the method was confirmed by the analysis of four water samples. The obtained results were concordant between the samples and spiked samples concentrations.

3.7. Understanding the role of ARS

The complexes of Pb(II) [61], Cd(II) [62], and Bi(III) [63] with ARS have been reported in stoichiometric ratios of 1:1, 1:2, and 1:3, respectively. Using a 30.0 µmol L^{-1} acetic acid solution, the UV–Vis spectra of a 162.0 µmol L^{-1} ARS solution in the absence and in the presence of either Pb(II), Cd(II), or Bi(III) in a 1:5 (metal:ligand) molar ratio were measured. Fig. S5 shows the UV–Vis spectra. The absorption of the ligand was observed at 421 nm (λ_{max}). A second band or shoulder was observed between 512 and 540 nm due to the addition of metal ions, and this band was related to the particular complex formed.

The role of ARS in the electrochemical response of lead and cadmium was studied in the absence and in the presence of ARS (Fig. 4). First, the bismuth film was deposited. Second, the electrode was
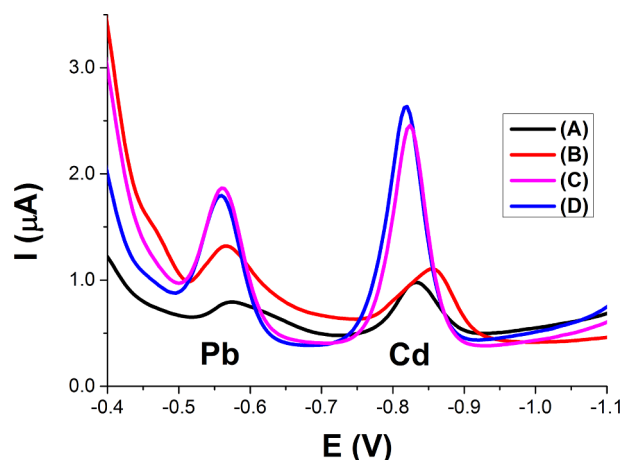

Fig. 4. Effect of the presence of ARS on the bismuth film formation and on the Pb(II) and Cd(II) deposition. Conditions: $[CH_3COOH]$: 30.0 mmol L^{-1}; $[Bi(III)]$: 0.75 mg L^{-1}; $[Fe(CN)_6^{4-}]$: 50.0 µmol L^{-1}; $[Pb(II)]$ and $[Cd(II)]$: 20.0 µg L^{-1}; E_{dep}: −1.40 V. (A) Bi(III), Pb(II) and Cd(II) deposition: t_{dep}: 60 s. (B) Bi(III) deposition: t_{dep}: 60 s; Pb(II) and Cd(II) deposition: $[ARS]$: 40.0 µmol L^{-1}, t_{dep}: 60 s. (C) Bi(III) deposition: $[ARS]$: 40.0 µmol L^{-1}, t_{dep}: 60 s; Pb(II) and Cd(II) deposition: t_{dep}: 60 s. (D) Bi(III), Pb(II) and Cd(II) deposition: $[ARS]$: 40.0 µmol L^{-1}, t_{dep}: 60 s.

immersed in a new solution, and the deposition of Pb(II) and Cd(II) was performed. In each step, a deposition time of 60 s was applied. The presence of ARS during the formation of the bismuth film generated an increase of the analytical response. However, in the second step, the presence of ARS did not generate an important signals variation. Therefore, the positive effect of ARS was related to the film formation rather than in the deposition of Pb(II) and Cd(II).

FESEM micrographs of the bismuth films deposited in an acetic acid medium in the absence and in the presence of ARS and using a 0.1 mol L^{-1} acetate buffer solution (pH 4.5) were obtained (Fig. S6). No significant differences were found between the formed deposits. From the micrographs, it was possible to observe that a large area of the glassy carbon electrode was covered with bismuth for the deposit formed in the presence of ARS. The greater amount of deposited bismuth can explain the increase of the sensitivity of the method. However, investigation of the surfaces by using energy dispersive X ray spectroscopy did not detect more deposited bismuth. The percentage of bismuth on the electrode surface was 0.11% for the three depositions. This result did not agree with the visual analysis of the micrographs.

Additional electrochemical and surface characterization studies of

the bismuth film electrode are required to understand the effect of ARS. It is out of the scope of this work, and we expect to study this behaviour in future efforts.

4. Conclusions

The developed method allows for quantification of Pb(II) and Cd(II) in freshwater samples with concentrations of less than 1.0 μg L^{-1}. The presence of ARS increases the sensitivity of the method. Therefore, either the achieved detection limits were lower than the detection limits reported in previous works or the deposition time required to accomplish the same order of concentrations was shorter. An exhaustive interference study was performed. This investigation included many ions whose effects have not been studied previously. The accuracy and the applicability of the method were demonstrated by the analysis of two certified reference materials and four freshwater samples, all with satisfactory results. The effect of the ARS on the sensitivity of the method was studied. Until now, the results that have been obtained suggested that the role of ARS was more related to the bismuth film formation than deposition of the analytes. Future experiments and studies will be performed to gain better understanding of the role of ARS and these experiments will include electrochemical and surface film characterization studies.

CRediT authorship contribution statement

Carlos Rojas-Romo: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Visualization, Supervision, Project administration, Funding acquisition. **Margarita E. Aliaga:** Conceptualization, Methodology, Resources, Supervision. **Verónica Arancibia:** Conceptualization, Methodology, Resources, Supervision. **Marisol Gomez:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2020.105373.

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