



# Chronoamperometric determination of lead ions using PEDOT: PSS modified carbon electrodes

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## ABSTRACT

A new simple chronoamperometry methodology was developed for the ultrasensitive determination of lead ions using a PEDOT:PSS coated graphite carbon electrode. The polymer was directly coated on a graphite carbon electrode and characterized using simple cycle voltammetric measurements. The presence of lead ions induced a cathodic peak starting at  $-550 \pm 10$  mV vs. Ag/AgCl, and an anodic peak starting at  $-360 \pm 10$  mV vs. Ag/AgCl. Electroaccumulation of lead ions onto the PEDOT:PSS modified electrode was performed at  $-650$  mV vs. Ag/AgCl for 30 s in a pH 2.2 hydrochloric acid solution. Chronoamperometry measurements were carried out at  $-350$  mV vs. Ag/AgCl allowing the oxidation of accumulated lead. Using this method, lead ions were detected for concentrations ranging between  $2.0 \text{ nmol L}^{-1}$  and  $0.1 \text{ } \mu\text{mol L}^{-1}$  ( $R^2 = 0.999$ ). The detection limit was calculated to be  $0.19 \text{ nmol L}^{-1}$  and the quantification limit of  $0.63 \text{ nmol L}^{-1}$ . The method was shown to be highly precise and sensitive, negligible interference was detected from other metal ions. The proposed method was successfully applied for the detection of lead ions in vegetables.

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## 1. Introduction

The detection of heavy metal ions in aqueous solutions plays an important role in the field of environmental and industrial water analysis [1]. Among these metal ions,  $\text{Pb}^{2+}$  has always been an important target due to its adverse effects on health and environment [2]. Although many regulations have been set worldwide to control the spread of lead containing products, accumulation of this material in soil or river sediments represent a major source for crops contamination.

The certified analytical methods for heavy metals monitoring are based on electrothermal atomic absorption spectrometry (ET-AAS) [3], flame atomic absorption spectrometry (FAAS) [4], inductively coupled plasma mass spectrometry (ICP-MS) [5], and inductively coupled plasma optical emission spectrometry (ICP-OES) [6]. Despite these methods have shown for many years their efficiency, they are quite expensive and involve extensive preparation steps which are not adapted for *in situ* and real time monitoring [7].

The search for new and cheap chemical sensors for heavy metal ions is currently of prime importance for *in situ* reliable analytical determination or simultaneous monitoring in both environmental and biological fields [8]. Electrochemical techniques using chemically modified electrodes have shown their great potential to meet this demand, leading to sensors with high sensitivity and reliability [9,10].

In 2008, Manisankar et al. developed voltammetric sensors using seven polymer modified glassy carbon electrodes that utilized for the determination of heavy metals, and reported a very low detection limits by using the poly(3,4-ethylenedioxythiophene) (PEDOT) [11]. This extremely promising material was traditionally synthesized by oxidation of monomer in the presence of a strong oxidant which showed high insolubility and intractability [12], but this inconvenience was overcome using a polymer electrolyte such as poly(styrenesulfonate) (PSS) in the reaction media [13]. PEDOT:PSS dispersions consist of a conducting poly(3,4-ethylenedioxythiophene) polycation (PEDOT) and a poly(styrenesulfonate) polyanion (PSS) that acts as a counter poly-ion and stabilizer keeping the PEDOT chain dispersed in the aqueous medium. PEDOT–PSS polymers are generally deposited as thin film directly on the surface of the transducer by solvent casting, dip-coating, spin-coating [14] or inkjet microdeposition [15].

In this work, a simple and directly modified PEDOT:PSS graphite electrode is presented as a new sensor for the determination of lead. The detection is performed in two steps consisting of elec-

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troaccumulation of the lead ions on the electrode surface followed by a chronoamperometric anodic detection. The potentiality of the described method for detecting lead in environmental samples is also reported.

## 2. Material and methods

### 2.1. Reagents

Poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesized by Cidotec (San Sebastian, Spain) according to a previously described method [16].

Supporting electrolytes were prepared in bidistilled water using nitric acid ( $\text{HNO}_3$ , 65%), citric acid anhydrate crystals ( $\text{C}_6\text{H}_8\text{O}_7$ ), sodium chlorite ( $\text{NaCl}$ ), sodium acetate ( $\text{CH}_3\text{COONa}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ , 99.5%) and hydrochloric acid ( $\text{HCl}$ , 37%), all purchased from Merck Chemicals.

A  $10^{-2} \text{ mol L}^{-1}$  lead stock solution was prepared from reagent grade lead nitrate  $\text{Pb}(\text{NO}_3)_2$  (Merck chemicals). Interference studies of cationic ions were made by adding an indicated quantity of the corresponding nitrate salts, except for arsenic solution which was prepared from sodium arsenite ( $\text{NaAsO}_2$ ), all these salts were purchased from Merck chemicals.

### 2.2. Carbon electrode preparation and modification

Graphite carbon electrode rods with diameter  $\varnothing = 0.945 \text{ cm}$  was purchased from Thermadyne, Arcair (Tweco Inc.). The electrode rod was molded in surround with 50% (w/v) self curing copolymer acrylic resin (RESPAL, Type II – class I, Italy), allowing the cross-cutting of the uncovered graphite rod as a carbon electrode with a contact surface area of  $0.708 \text{ cm}^2$ . Electrodes prepared in this way were used as counter electrode and, after modification, as working electrode. Prior to each experiment, the carbon electrode was successively polished, rinsed with deionized water, and ultrasonicated in a 1:1 aqueous solution of  $\text{HCl}$  and ethanol solution for 2 min, the process was then followed with air drying.

Modified working electrodes were prepared by direct coating of the carbon electrode with the PEDOT:PSS dispersion, and left to dry for 30 min at  $60^\circ\text{C}$ . The study of the influence of PEDOT:PSS loadings was made by using various amounts of PEDOT:PSS, namely 10, 20, 40, 60, 80, 100, or  $120 \mu\text{L}$  to coat the surface of seven identical working carbon electrodes.

### 2.3. Apparatus and measurement

Electrochemical measurements were performed with a VOLTALAB potentiostat (model PGP 201, Radiometer, France), driven by the general purpose electrochemical systems data processing software (VOLTALAB master 4 software) connected with proper computation system. The electrolysis vessel with volume capacity of 100 mL, was connected to a three electrode system consisting of a PEDOT:PSS modified carbon electrode, a carbon counter electrode and an  $\text{Ag}/\text{AgCl}$  double junction reference electrode (model, AG 9101, Metrohm, Switzerland, with 3 M  $\text{KCl}$  filling).

The modified electrode was tested in 25 mL electrolyte under constant magnetic stirring (400 rpm) and was kept thermostated at  $25^\circ\text{C}$  (any modification of these conditions should be otherwise stated).

A Hitachi Atomic Absorption Spectrophotometry (AAS), Z-2000 Series, was used to validate the lead determination method. The AAS system was provided with hollow cathod lamp (Hitachi) for lead determination, and the instrument run under the following measuring conditions: wavelength 283.3 nm, lamp current 6 mA, acetylene fuel at flow rate  $2.0 \text{ L min}^{-1}$ , and burner height 7.5 mm.

A digital pH-meter from Wissenschaftlich Technische Werkstätten (Inolab level 1, Germany), was used for pH values reading.

### 2.4. Cyclic voltammetry measurements

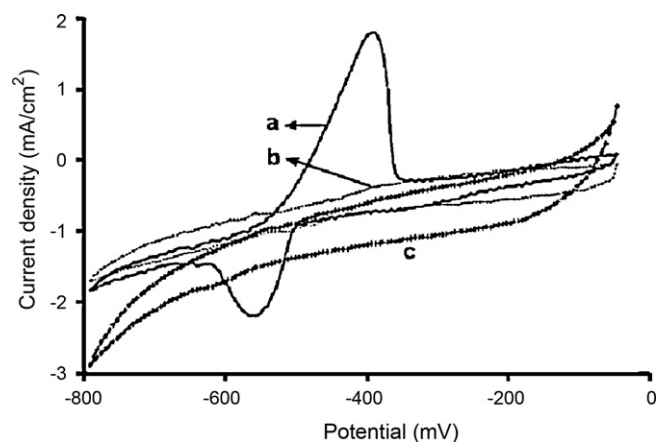
Cyclic voltammetry measurements were performed by scanning the potential from 0.0 V to  $-0.8 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  at a scan rate of  $10 \text{ mV s}^{-1}$ . The oxidation peak was generated upon injection of lead ions to the final concentration of  $0.25 \text{ mmol L}^{-1}$ .

### 2.5. Chronoamperometric measurements

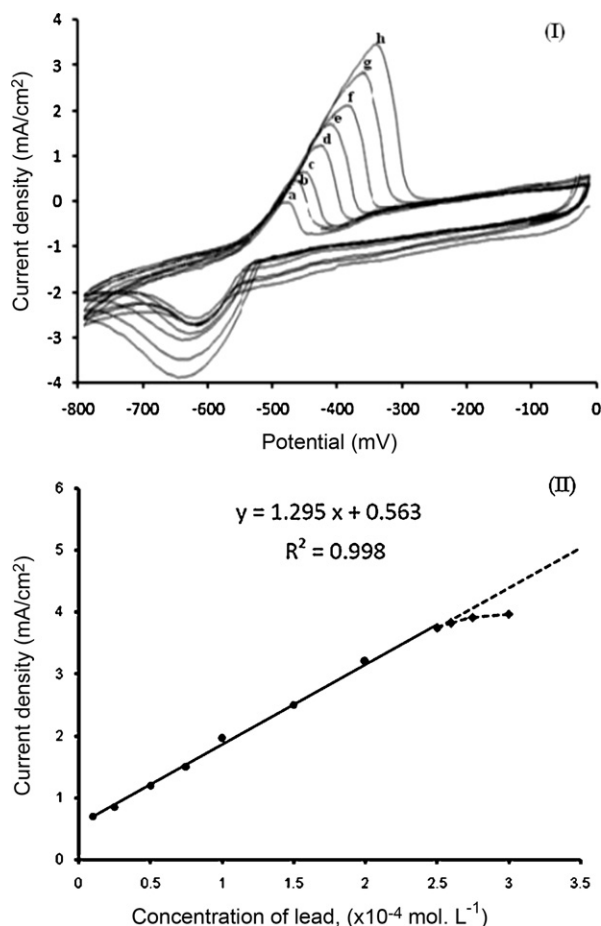
A preliminary deposition step was carried out by applying a reduction voltage at  $-650 \text{ mV}$  vs.  $\text{Ag}/\text{AgCl}$  for 30 s, allowing a maximum deposition of lead ions on the working electrode. Chronoamperometric measurements were then performed by automatically switching the applied potential to an anodic value of  $-350 \text{ mV}$  vs.  $\text{Ag}/\text{AgCl}$ . The time necessary to reach oxidation current density plateau was 3–15 s. The peak response for the current intensity at the voltage corresponded to the anodic values are concentration dependent. A calibration curve for lead ion concentration ( $\text{nmol L}^{-1}$ ) against the peak current density ( $\text{mA/cm}^2$ ) was then constructed.

### 2.6. Pretreatment of the vegetable samples

Vegetables of chard (white beet), spinach and mint were collected from the countryside area of Quweiq river mouth (Aleppo, Syria). The vegetable was collected, washed, dried for 24 h at  $105^\circ\text{C}$ , and then 9 grams of each vegetable were incinerated at  $500^\circ\text{C}$  for 6 h. The white ash obtained was dissolved in 10 mL solution of  $6 \text{ mol L}^{-1}$  nitric acid, with warming to insure the dissolution of metal ions. The solution was then filtered and the filter was washed with 10 mL of  $6 \text{ mol L}^{-1}$  nitric acid, finally the filtrates were combined and adjusted to a final volume of 25 mL. The obtained solution was analyzed by atomic absorption spectroscopy. Chronoamperometric measurements were carried out using 1 mL of the obtained solution diluted to 100 mL with  $0.05 \text{ mol L}^{-1}$   $\text{HCl}$ . Calibration measurements were performed using 1 mL of the same solution diluted to 100 mL with lead solutions of known concentrations.



**Fig. 1.** Cyclic voltammograms for lead ion  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  in  $0.05 \text{ mol L}^{-1}$   $\text{HCl}$  on: (a) PEDOT:PSS modified carbon electrode, and (b) bare carbon electrode, comparing with (c) lead free electrolyte on PEDOT:PSS modified carbon electrode. Potential ramp 0.0 V to  $-0.8 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ , scan rate  $10 \text{ mV s}^{-1}$ .



**Fig. 2.** (I) Cyclic voltammogram and (II) the corresponded calibration curve, in 0.05 mol L<sup>-1</sup> HCl medium, using PEDOT:PSS modified carbon electrode for lead ion concentration at: (a) 0.01, (b) 0.025, (c) 0.05, (d) 0.075, (e) 0.10, (f) 0.15, (g) 0.20 and (h) 0.25 mmol L<sup>-1</sup>. The potential ramp from 0.0 V to -0.8 V vs. Ag/AgCl at a scan rate of 10 mV s<sup>-1</sup>.

### 3. Results and discussion

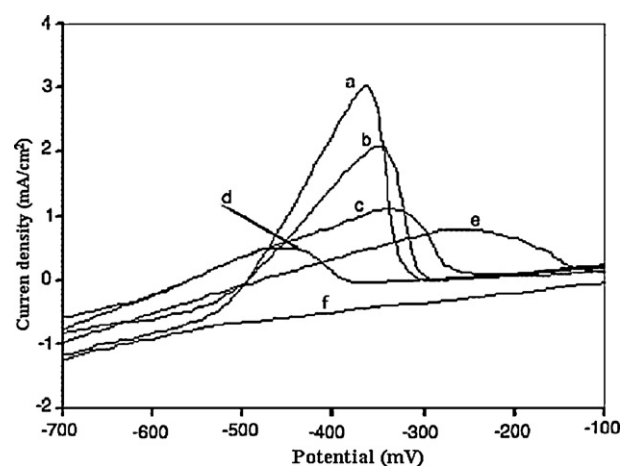
#### 3.1. Cyclic voltammetry experiments

Cyclic voltammograms of Pb<sup>2+</sup> on bare carbon electrode and PEDOT:PSS modified carbon electrodes were examined in 0.05 mol L<sup>-1</sup> HCl medium (Fig. 1).

No peak current was observed at bare carbon electrode (curve b), whereas on PEDOT:PSS modified carbon electrodes (curve a) Pb<sup>2+</sup> exhibits a narrow, well-defined anodic peak and a broad corresponding reduction peak, starting respectively at  $-360 \pm 10$  mV and  $-550 \pm 10$  mV vs. Ag/AgCl. No detectable signal was observed in the absence of Pb<sup>2+</sup> using the same electrolyte (curve c). These results showed the potential application of PEDOT:PSS modified electrode for detecting of lead ions. It was confirmed by studying the response of PEDOT:PSS modified carbon electrodes towards lead at various concentrations (Fig. 2I). The calibration curve demonstrated that the response was linear for all the Pb<sup>2+</sup> concentrations tested, i.e. from 0.01 to 0.25 mmol L<sup>-1</sup> ( $R^2 = 0.998$ ) (Fig. 2II).

#### 3.2. Optimization of experimental conditions

Optimum conditions for the electrochemical response of PEDOT:PSS modified carbon electrode were studied by measuring the anodic current density peak as a function of supporting electrolyte, concentration of supporting electrolyte, and PEDOT:PSS



**Fig. 3.** Sweep voltammograms extracted from cyclic voltammograms on PEDOT:PSS modified carbon electrode for  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> lead ion in: (a) HCl, (b) HNO<sub>3</sub>, (c) CH<sub>3</sub>COONa, (d) NaCl, (e) C<sub>6</sub>H<sub>7</sub>O<sub>8</sub> and (f) CH<sub>3</sub>COOH, all at concentration of 0.05 mol L<sup>-1</sup>. The potential ramp from 0.0 V to -0.8 V vs. Ag/AgCl at a scan rate of 10 mV s<sup>-1</sup>.

loading. The stability of PEDOT:PSS coating material in the supporting electrolyte was also investigated.

#### 3.2.1. Effect of supporting electrolyte

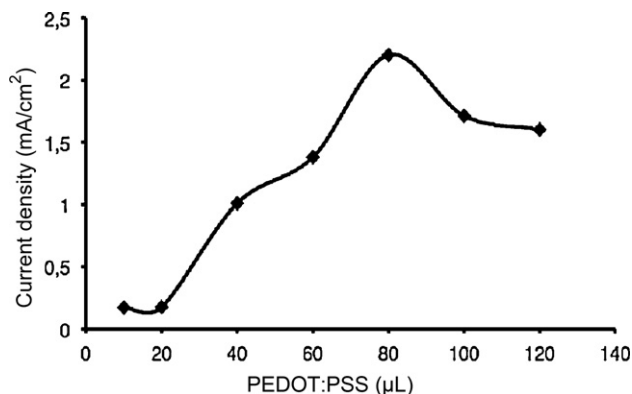
Sweep voltammograms extracted from the cyclic voltammograms obtained in the presence of  $10^{-4}$  mol L<sup>-1</sup> Pb<sup>2+</sup> in 0.05 mol L<sup>-1</sup> of various electrolytes (HCl, HNO<sub>3</sub>, C<sub>6</sub>H<sub>7</sub>O<sub>8</sub>, NaCl, CH<sub>3</sub>COOH, and CH<sub>3</sub>COONa) are presented in Fig. 3.

The highest and narrowest peak was surprisingly observed in HCl medium (pH = 2.2). Similar results with lower anodic current were obtained with nitric acid, whereas a dramatic reduction of the analytical signal was observed using the other electrolytes, no sign being observed in acetic acid.

HCl was thus used as supporting electrolyte for subsequent experiments, using concentrations ranging from  $10^{-4}$  mol L<sup>-1</sup> to 0.4 mol L<sup>-1</sup>. In these conditions a maximum anodic current response was observed in 0.05 mol L<sup>-1</sup> HCl, with sharp and reproducible analytical signals. This electrolyte concentration was therefore used in further optimization studies.

#### 3.2.2. Effect of PEDOT:PSS loading

Electrodes were modified using several PEDOT:PSS loads and then tested for the determination of  $10^{-4}$  mol L<sup>-1</sup> Pb<sup>2+</sup>. The current density peaks obtained with each type of electrode are reported in Fig. 4. It was observed that the current density increases with the loading volume and reaches a maximum value for a PEDOT:PSS



**Fig. 4.** The effect of PEDOT:PSS loading against the anodic current density peaks for  $10^{-4}$  mol L<sup>-1</sup> lead ions detection.

**Table 1**Chronoamperometric determination of  $\text{Pb}^{2+}$  ions on PEDOT:PSS-modified carbon electrode in  $\text{HCl}$   $0.05 \text{ mol L}^{-1}$  media.

$\text{Pb}^{2+}$ ( $\times 10^{-9} \text{ mol L}^{-1}$ )	Intra-day accuracy and precision			Inter-day accuracy and precision		
	$\text{Pb}^{2+}$ ( $\times 10^{-9} \text{ mol L}^{-1}$ ) ( $n=6$ )			$\text{Pb}^{2+}$ ( $\times 10^{-9} \text{ mol L}^{-1}$ ) ( $n=5$ )		
	Found $\pm$ SD	R (%)	RSD (%)	Found $\pm$ SD	R (%)	RSD (%)
1.00	$0.98 \pm 0.04$	98.00	4.08	$0.97 \pm 0.04$	97.50	4.31
5.00	$4.98 \pm 0.17$	98.62	3.41	$4.90 \pm 0.18$	98.08	3.51
10.00	$9.95 \pm 0.31$	99.50	3.11	$9.85 \pm 0.33$	98.48	3.43
20.00	$20.01 \pm 0.46$	100.05	2.29	$19.83 \pm 0.51$	99.14	2.49
40.00	$40.42 \pm 0.74$	101.05	1.83	$39.94 \pm 0.85$	99.84	2.16
60.00	$60.30 \pm 0.95$	100.50	1.57	$59.91 \pm 1.12$	99.85	1.84
80.00	$79.74 \pm 1.12$	99.67	1.40	$79.27 \pm 1.35$	99.09	1.54
100.00	$100.28 \pm 1.25$	100.28	1.24	$99.89 \pm 1.54$	99.89	1.54

loading of  $80 \mu\text{L}$ . The decrease of current density was observed using higher loading volumes, probably due to a reduction in the conductivity of the coated membrane as the thickness of PEDOT:PSS increases. Thus, PEDOT:PSS loading volume of  $80 \mu\text{L}$  was selected and used in further studies.

### 3.2.3. Stability of PEDOT:PSS modified carbon electrodes

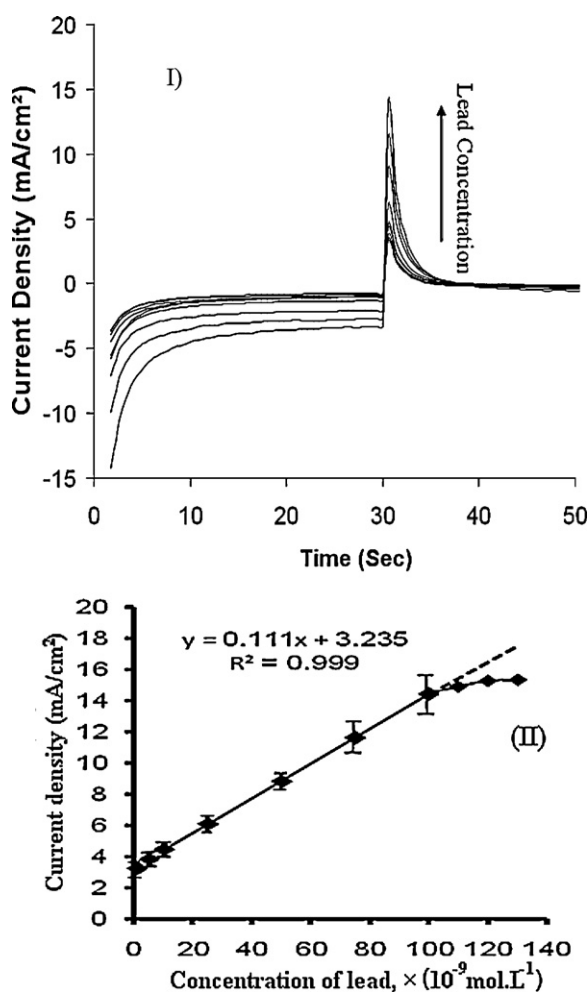
A good stability of chemically modified electrodes is a key condition for the reliability of the sensors. The stability of the PEDOT:PSS modified carbon electrodes described in this work was

studied by keeping the electrode immersed in  $0.05 \text{ mol L}^{-1}$   $\text{HCl}$  solution for several days, at room temperature ( $25^\circ\text{C}$ ). During this time, the electrode was tested daily using  $10^{-4} \text{ mol L}^{-1}$  of lead ions. In these conditions, the peak response for the anodic current density showed a good stability during the first 10 days ( $2.428 \pm 0.042 \text{ mA/cm}^2$ ), with RSD values in day 10 is 4.0% ( $n=5$ ). The response decreased slightly at day 11 (RSD = 5.2%;  $n=5$ ).

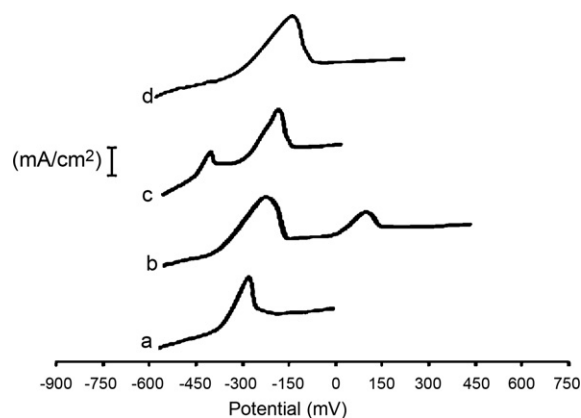
### 3.3. Chronoamperometric measurements

Chronoamperometric measurements of PEDOT–PSS modified sensors were carried out in the conditions optimized by voltammetric measurements, i.e. using a  $80 \mu\text{L}$  PEDOT:PSS loading and  $0.05 \text{ mol L}^{-1}$   $\text{HCl}$  as supporting electrolyte. Prior of measurements, an electrodeposition step was performed for 30 s, allowing an optimal deposition of lead ions on the working electrode. The chronoamperometric response of the sensor achieved using various lead ions concentrations is presented in Fig. 5. A strictly linear variation of the anodic peak current was observed for concentrations ranging from  $2.0 \times 10^{-9} \text{ mol L}^{-1}$  to  $1.0 \times 10^{-7} \text{ mol L}^{-1}$  ( $y = 0.111x + 3.352$ ,  $R^2 = 0.999$ ). The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the formula  $\text{LOD} = 3.3 \text{ SD/b}$  and  $\text{LOQ} = 10 \text{ SD/b}$ , respectively, where SD is the standard deviation of five reagent blank determinations and b is the slope of the calibration curve [17]. In these conditions, the LOD and LOQ of the developed sensor were calculated to be  $0.19 \text{ nmol L}^{-1}$  and  $0.63 \text{ nmol L}^{-1}$ , respectively.

It was observed that lead concentrations higher than  $0.1 \mu\text{mol L}^{-1}$  induced the formation of multilayers on the working



**Fig. 5.** (I) Chronoamperometric diagram and (II) the corresponded calibration curve, in  $0.05 \text{ mol L}^{-1}$   $\text{HCl}$  medium, using PEDOT:PSS modified carbon electrode for lead ion concentration at: 1, 5, 10, 20, 40, 60, 80, 100, 120 and  $140 \text{ nmol L}^{-1}$ . The reduction voltage  $-650 \text{ mV}$  vs.  $\text{Ag/AgCl}$  for 30 s then switched to an oxidation voltage of  $-350 \text{ mV}$  vs.  $\text{Ag/AgCl}$ .



**Fig. 6.** Sweep voltammograms extracted from cyclic voltammograms obtained from  $0.05 \text{ mol L}^{-1}$   $\text{HCl}$  solution containing: (a)  $\text{Pb}^{2+}$  alone, (b)  $\text{Pb}^{2+}$  with  $\text{Cu}^{2+}$ , (c)  $\text{Pb}^{2+}$  with  $\text{Cd}^{2+}$  and (d)  $\text{Pb}^{2+}$  with  $\text{Sn}^{2+}$ , on PEDOT:PSS modified carbon electrode at  $0.1 \text{ mmol L}^{-1}$  for each individual metal ions concentration. The potential ramp from  $0.0 \text{ V}$  to  $-0.8 \text{ V}$  vs.  $\text{Ag/AgCl}$  at a scan rate of  $10 \text{ mV s}^{-1}$ .



**Table 2**Effect of other metal ions on the chronoamperometric determination of  $1.0 \times 10^{-8} \text{ mol L}^{-1} \text{ Pb}^{2+}$  on PEDOT:PSS modified carbon electrode.

Added ions	Pb <sup>2+</sup> concentration			Variation (%) <sup>a</sup>	Tolerable limit [cation]/[Pb <sup>2+</sup> ]
	Mean ( $10^{-8} \text{ mol L}^{-1}$ )	SD ( $10^{-8} \text{ mol L}^{-1}$ )	RSD (%)		
Alone	1.02	0.01	1.3	0.0	0
Zn <sup>2+</sup>	1.06	0.02	2.2	+3.9	900
Fe <sup>3+</sup>	0.99	0.03	2.7	−2.3	1000
Cu <sup>2+</sup>	1.10	0.03	3.5	+7.8	300
Cd <sup>2+</sup>	0.98	0.01	1.1	−3.9	950
Hg <sup>2+</sup>	1.00	0.01	0.9	−1.9	900
Ca <sup>2+</sup>	1.08	0.03	3.1	+5.6	750
As <sup>3+</sup>	0.99	0.04	4.5	−4.9	1000
Ni <sup>2+</sup>	1.05	0.02	2.3	+2.3	5000
Sn <sup>2+</sup>	1.09	0.04	4.1	+6.9	500

<sup>a</sup> Variation (%) at  $1.10^{-8} \text{ mol L}^{-1} = 100 \times [(\text{peak current of pure lead}) - (\text{peak current of lead with each cations})]/(\text{peak current of pure lead})$ .

electrode surface, resulting in a slight decrease of the peak current and therefore affecting the detection procedure.

The precision and accuracy of the method towards lead determination was assessed by analyzing 8 standard solutions of lead ions with concentrations ranging from  $1.0 \text{ nmol L}^{-1}$  to  $100.0 \text{ nmol L}^{-1}$  in  $0.05 \text{ mol L}^{-1} \text{ HCl}$  (Table 1). Whatever the value of tested concentration is, a very accurate quantitative recovery was obtained, with rates ranging from 98% to 101.05%, intra-day RSD values  $\leq 4.31$  ( $n = 6$ ), and inter day RSD values  $\leq 4.03\%$  ( $n = 5$ ).

The intervariability of the sensors responses was studied by measuring the response of 6 different electrodes to  $40.0 \text{ nmol L}^{-1}$  lead ions. In these conditions, a very satisfying RSD value of 2.13% was obtained. These results showed excellent reproducibility of PEDOT:PSS modified carbon electrodes.

#### 3.4. Study of interferences due to other metallic ions

The influence of other metal ions (Zn<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Ca<sup>2+</sup>, As<sup>3+</sup>, Sn<sup>2+</sup> and Hg<sup>2+</sup>) on the determination of  $1.0 \times 10^{-8} \text{ mol L}^{-1} \text{ Pb}^{2+}$  in  $0.05 \text{ mol L}^{-1} \text{ HCl}$  was investigated. The experiment data are listed in Table 2. A relative error of  $\pm 5\%$  on the concentration of Pb<sup>2+</sup> was considered as tolerable.

The results indicated that in our working conditions most of the metal ions do not interfere on the determination of Pb<sup>2+</sup>, except Cu<sup>2+</sup> that displayed an oxidation peak at +75 mV vs. Ag/AgCl for high concentration levels, up to 300 fold higher than Pb<sup>2+</sup> concentration. The same behavior was observed for Sn<sup>2+</sup> ions at concentration levels exceeding 500 fold, as shown in pre-experimental cyclic voltammetry studies of combined Sn<sup>2+</sup> and Pb<sup>2+</sup> solutions. Fig. 6 shows the sweep voltammograms extracted from cyclic voltammograms obtained from  $0.05 \text{ mol L}^{-1} \text{ HCl}$  solutions containing Pb<sup>2+</sup> ( $0.1 \text{ mmol L}^{-1}$ ), with or without  $0.1 \text{ mmol L}^{-1}$  of Cu<sup>2+</sup>, Cd<sup>2+</sup>, or Sn<sup>2+</sup>.

It was shown that the peak current of Pb<sup>2+</sup> oxidation was not significantly varied in the presence of more than 900 fold higher concentrations of Zn<sup>2+</sup>, Fe<sup>3+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, As<sup>3+</sup> or Ni<sup>2+</sup> ions. The above results demonstrate that at optimum working conditions the PEDOT:PSS modified carbon electrode showed good sensitivity for the detection of Pb<sup>2+</sup> as well as very good selectivity towards other metallic ions.

#### 3.5. Application to real samples

The PEDOT:PSS modified carbon electrode was used for the determination of lead ions in three different vegetables (chard, spinach, and mint) that have been cultivated in an area well-known to be contaminated by lead [3].

The results shown in Table 3 clearly demonstrate the presence of lead in the three different vegetable samples. The analytical

**Table 3**Chronoamperometric determination of lead in different vegetable samples spiked with known concentrations of Pb<sup>2+</sup>.

Sample	Pb <sup>2+</sup> added ( $\times 10^{-8} \text{ mol L}^{-1}$ )	Pb <sup>2+</sup> found $\pm$ SD ( $\times 10^{-8} \text{ mol L}^{-1}$ ) ( $n = 5$ )	R (%) <sup>a</sup>
Chard	–	$4.60 \pm 0.04$	–
	2.5	$7.06 \pm 0.08$	98.40
	5.0	$9.69 \pm 0.09$	99.01
	7.5	$12.06 \pm 0.11$	99.50
Spinach	–	$4.20 \pm 0.05$	–
	2.5	$6.67 \pm 0.07$	98.84
	5.0	$9.15 \pm 0.09$	98.97
	7.5	$11.63 \pm 0.11$	99.07
Mint	–	$4.1 \pm 0.04$	–
	2.5	$6.58 \pm 0.07$	99.34
	5.0	$9.1 \pm 0.08$	99.97
	7.5	$11.6 \pm 0.11$	100.04

<sup>a</sup>The recovery values for added Pb<sup>2+</sup> concentrations ( $n = 5$ ).

results obtained from a series of lead standard solutions spiked with unknown samples gave quantitative recoveries in the range of 98.4–100.4%. The amount of lead in unknown samples was also determined and was expressed as the mass fraction of dried vegetable (Table 4). The test of significance showed that Student's *t*-test values and *F*-values at 95% confidence level were less than the theoretical values, indicating that there is a good agreement between the results obtained by the proposed method and the reference AAS method. These results prove that the PEDOT:PSS modified carbon electrode developed in this work has practical significance and is able to determine Pb<sup>2+</sup> in real samples.

Moreover, the concentration levels of Pb<sup>2+</sup> in the three vegetable samples analyzed indicate high levels of contamination that demand more attention and control of the pollution in the region.

**Table 4**Determination of Pb<sup>2+</sup> ions in vegetable samples, comparison of chronoamperometric and atomic absorption spectrometry methods. The tabulated *t* and *F* values at 95% confidence level and for four degrees of freedom were respectively 2.78 and 6.39.

Sample	Pb <sup>2+</sup> ( $\mu\text{g/g}$ ) $\pm$ SD	
	Chronoamperometric method ( $n = 5$ )	Atomic absorption spectrometry method ( $n = 5$ )
Chard	$2.45 \pm 0.05$	$2.36 \pm 0.09$ $F = 4.00$ $t = -2.16$
Spinach	$2.41 \pm 0.05$	$2.46 \pm 0.09$ $F = 3.24$ $t = +1.11$
Mint	$2.35 \pm 0.04$	$2.40 \pm 0.07$ $F = 3.53$ $t = +1.72$

#### 4. Conclusion

Fast and effective analyses of lead ions in batch water samples have been performed using a novative chronoamperometric monitoring method involving PEDOT:PSS modified carbon electrodes. The cyclic voltammetry results clearly showed the advantages of PEDOT:PSS coated electrodes as compared with bare carbon electrodes. The polymer coating allows avoiding problems of irreversible adherence, which otherwise could lead to blocking and fouling of the electrode surface. The PEDOT:PSS modified carbon electrode showed excellent responses with LOD values in the nanomolar ( $\mu\text{g L}^{-1}$ ) level. The suitability of the proposed method was demonstrated by determining the concentration of lead in vegetable samples grown in a lead contaminated area, the validation of the results was performed by atomic absorption spectroscopy measurements.

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