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on the occasion of his 95th anniversary

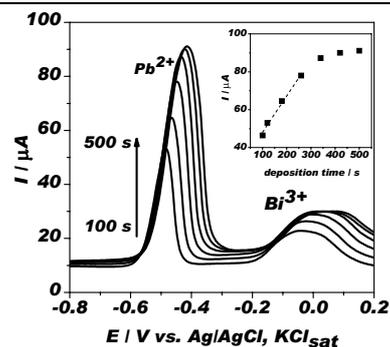
CARBON PASTE ELECTRODE MODIFIED WITH Bi NANOPARTICLES - CARBON XEROGEL FOR Pb²⁺ DETERMINATION BY SQUARE WAVE ANODIC STRIPPING VOLTAMMETRY

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A new composite electrode consisting of carbon paste (CPE) modified with carbon xerogel containing Bi nanoparticles (BiCXe) is presented. The proposed electrode was used for the Pb²⁺ ions determination at trace levels by using square wave anodic stripping voltammetry (SWASV). The analytical parameters of BiCXe-CPE are satisfactory when compared with the maximum admissible concentration of 10 µg Pb²⁺/l required by the UE legislation for the drinking water. BiCXe-CPE electrode has been found sufficiently selective over the Pb²⁺ ions, so it can be applied not only to individual determination of Cd²⁺, but also to the simultaneous determination of Cd²⁺ and Pb²⁺.



INTRODUCTION

Lead is a very toxic metal, being harmful to nervous, immune, reproductive and gastrointestinal systems of living bodies. The limits set for the maximum allowable concentrations of lead in drinking water by World Health Organization are 10 µg/L.¹ Consequently, lead monitoring in food and in environment is of crucial importance.

One of the most powerful methods for determination of trace lead in various samples is the stripping analysis. In anodic stripping voltammetry (ASV), the analyte of interest is electrodeposited on the working electrode during a

reduction step, and oxidized from the electrode during the stripping step, the resulting current being measured.² The traditional electrode used for ASV measurements is the mercury electrode.³ However, due to its toxicity, new sensitive, non-toxic electrodes were developed to replace it. Among them, Bi-based electrodes are of particular interest due to their performances, which are comparable to those of Hg electrodes and to their negligible toxicity.⁴ The use of Bi electrodes in ASV is based on Bi ability to form low temperature alloys with heavy metals,⁵ favoring the accumulation of these ions during the preconcentration step of the stripping analysis.

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Bi based electrodes are using mainly Bi films deposited on different substrates,⁶⁻¹¹ bismuth nano-powders,¹²⁻¹⁴ bismuth-modified boron doped diamond¹⁵ and Bi containing composites, such as carbon paste doped *in situ* with bismuth-modified multi-walled carbon nanotubes.¹⁶

In this paper, a new composite electrode consisting of carbon paste (CPE) containing Bi-modified carbon xerogel (BiCXe) is presented. The carbon xerogel was prepared by sol-gel synthesis and it was impregnated with Bi³⁺, followed by gel washing, drying and thermal treatment. The BiCXe-CPE electrode successfully exploits the favourable electrochemical properties of carbon paste electrodes and combines them with the unique electroanalytical characteristics of Bi-based xerogels. The proposed electrode was used for the Pb²⁺ ions determination at trace levels by using square wave anodic stripping voltammetry (SWASV).

EXPERIMENTAL

Reagents

Resorcinol (98% purity, Aldrich), formaldehyde (37%, Merck, Germany), glycerol formal (98% purity, Sigma Aldrich), glacial acetic acids (100% purity Merck, Germany), NH₄OH (99% purity, Merck, Germany), bismuth nitrate (Bi(NO₃)₃ · 5H₂O, Alfa Aesar, UK) and distillate water were used.

Chemicals

Graphite powder and paraffin oil from Fluka and Sigma Aldrich were used to prepare the carbon paste electrodes. The buffer solution (0.1 M, pH 4.5) used in experiments was prepared by mixing appropriate volumes of 0.2 M sodium acetate (Reactivul-București, Roumania) with 0.2 M acetic acid (Merck, Germany). All aqueous solutions were prepared in double distilled water. Stock solution of 10⁻³ M of Pb²⁺ and Cd²⁺ were prepared by dissolving appropriate amounts of Pb(NO₃)₂ and Cd(NO₃)₂ · 4H₂O (Reactivul- București, Roumania) into the 0.1 M acetate buffer solution (pH 4). Standard solutions of Pb²⁺ and Cd²⁺ (10⁻⁷-10⁻⁵ M) were prepared by diluting the appropriate volumes of corresponding stock solution in the buffer solution.

Devices

All voltammetric measurements were performed using a PGSTAT 12/100, Booster 20A, electrochemical station (AUTOLAB, Holland). A pH-meter (MV 870 PRACITRONIC, Germany) equipped with a combined glass electrode was used to measure the pH of solutions. A three-electrode electrochemical cell consisting of a working electrode (carbon paste containing Bi-modified carbon xerogel, BiCXe-CPE) with inner diameter of 2 mm, a counter electrode of platinum, and a Ag/AgCl/KCl_{sat} reference electrode, have been used for all experimental measurements.

Preparation of Bi modified carbon xerogel

Bismuth salt (Bi³⁺) was dissolved in glycerol formal (GF) (0.12 g/mL). Resorcinol (R, 0.018 mole) and formaldehyde (F, 37%) were added under vigorous stirring to the previewed obtained solution (R/F = 0.5 molar ratio). As catalyst for polycondensation of resorcinol with formaldehyde, 10% NH₄OH (C) was added to the previous mixture (R/C = 1.8 mole). For pH correction acetic acids was added (Bi³⁺/AA = 0.1 g/mL). The solution was placed into tightly closed glass molds (7 cm-length x 1 cm internal diameter) and cured 3 days at 60°C. The resulting resorcinol-formaldehyde gel (RF-gels) impregnated with Bi³⁺ was washed with AA for 24 h and dried for 7 days in ambient conditions. The resulted Bi³⁺ impregnated organic xerogel was then pyrolysed at 550°C/Ar for 1h to obtain BiCXe.¹⁷

Preparation of the electrode

The obtained bars of CXe (blank) and BiCXe have been processed by crushing into a fine powder. Carbon paste electrodes (CXe-CPE and BiCXe-CPE) were prepared by homogenizing in a mortar by continuous hand-mixing for 30 min, 0.02 g graphite powder, 0.04 g CXe or BiCXe powder, and 30 μL paraffin oil. The composite paste was then introduced in a cylindrical holder having a 2 mm diameter. The carbon paste electrode surface was renewed before starting a new series of experiments or prior to analysis of each sample by extruding approximately 0.5 mm of carbon paste from the holder followed by wiping with wet filter paper. The electrode was ready to use, without any further electrochemical or chemical pretreatment.

Measurements procedure

Electrochemical tests, cyclic voltammetry (CV) and square wave voltammetry (SWV) were developed in a glass cell filled with 10 mL acetate buffer 0.1 M, pH 4.5. Before each experiment, a conditioning step was applied to the electrode surface at +0.3 V *vs.* Ag/AgCl, KCl_{sat} for 20 s, under stirring.

In SWV, the electrodeposition potential for lead and cadmium was -1.3 V *vs.* Ag/AgCl, KCl_{sat} for 120 s under stirring. Then, the stirring was stopped and, after a 10 s equilibration period, the voltammogram was recorded by applying a positive-going square wave stripping potential scan from -1.3 V to +0.5 V *vs.* Ag/AgCl, KCl_{sat}. The optimal parameters used in SWV (frequency of 25 Hz, pulse amplitude 50 mV, step increment 4 mV) were fixed after a systematic investigation of the electrochemical process. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Morpho-structural characterization

By analysis of N₂ adsorption-desorption isotherm it was established that the obtained composite BiCXe is microporous with BET surface area about 73 m²/g. The SEM investigations revealed the presence of spherical Bi nanoparticles with average diameter around 50 nm well dispersed in the porous carbon xerogel (Fig. 1). The XRD

pattern (Fig. 2) show the presence of two broad peaks at $2\theta \approx 24$ and 45° typical of the scattering of amorphous carbon and several narrow peaks, with

the most important at $2\theta \approx 27^\circ$ typical for the crystalline form of Bi.¹⁷

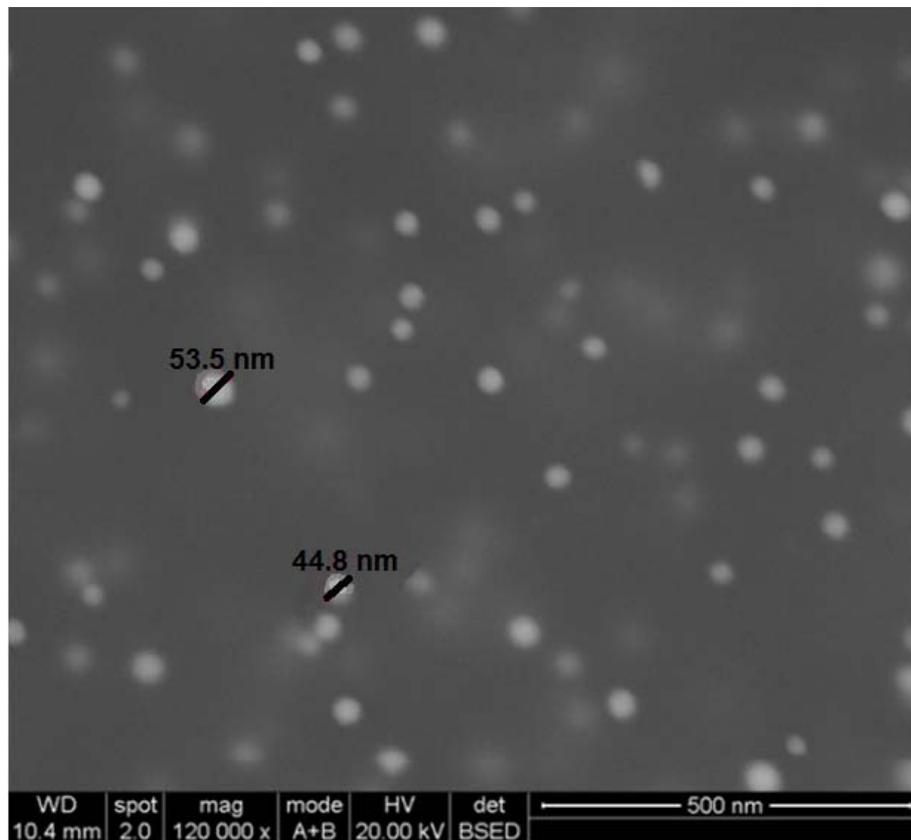


Fig. 1 – SEM image of Bi nanoparticles - carbon xerogel (BiCXe).

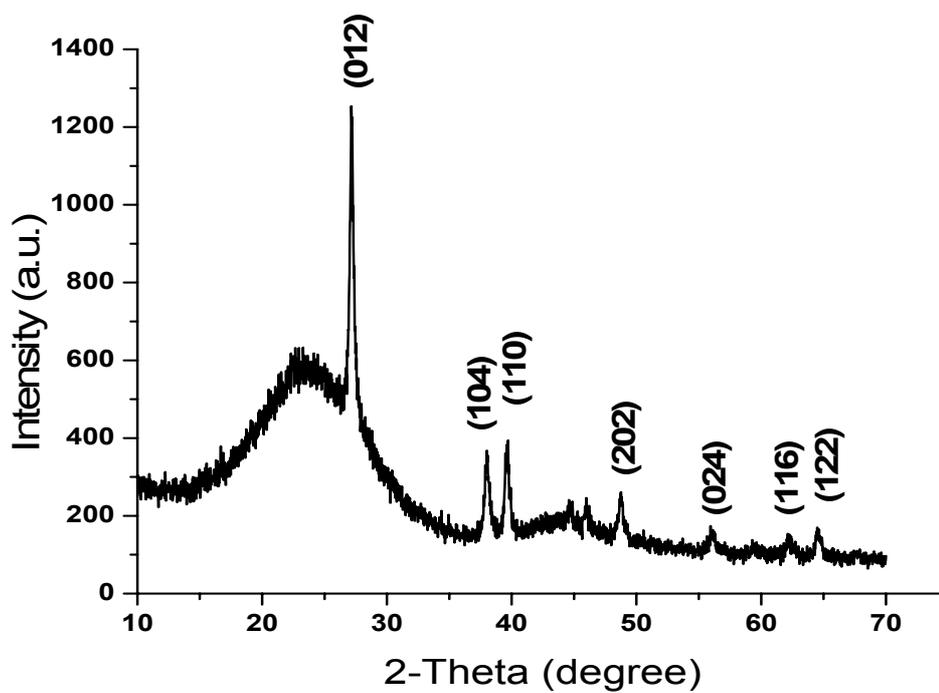


Fig. 2 – X-ray diffraction pattern of BiCXe.

Electrochemical characterization of BiCXe-CPE

The electrochemical behavior of the BiCXe-CPE was investigated by cyclic voltammetry or square wave voltammetry in acetate buffer (pH 4). The cyclic voltammogram recorded at BiCXe-CPE electrode (Fig. 3A) compared with the voltammogram at CXe-CPE electrode, show a good shaped pair of peaks attributed to the redox process of the Bi/Bi³⁺ within the Bi modified xerogel (BiCXe) present in the electrode composite matrix. Also, the higher background current observed at BiCXe-CPE than those recorded at CXe-CPE proves an increasing of the conducting properties of the BiCXe host matrix or an important differences between the porosity of the two compared electrode materials.¹⁸

The electrochemical parameters of the BiCXe-CPE electrode, estimated at a potential scan rate of 50 mV/s, were: anodic peak potential $E_{pa} = -0.05$ V (peak Ia); cathodic peak potential, $E_{pc} = -0.57$ V vs. Ag/AgCl, KCl_{sat} (peak Ic); formal potential, $E^{0'} = -0.310$ V vs. Ag/AgCl, KCl_{sat} (calculated as mean of E_{pa} and E_{pc}); the peak-to-peak potential separation, $\Delta E_p = -0.52$ V; and the ratio between the anodic and cathodic peak currents $I_{pa}/I_{pc} = 1.78$. These data lead to the conclusion that the redox electrode process is a quasi-reversible one. The values of the full width at half maximum

intensity of the anodic and cathodic peak currents ($\Delta E_{FWHM,a} = 0.190$ V, $\Delta E_{FWHM,c} = 0.200$ V), were much higher than the theoretical value ($90.5/n$ mV) expected for a surface confined redox couple involving the transfer of n electron.¹⁹ This great difference can be due either to some physical non-uniform repartition of the BiCXe into the electrode matrix or to the existence of repulsive interactions between the active redox centers.¹⁸

The same behavior is noticed during SWV measurements (Fig. 3B), when the oxidation peak I_a of the Bi/Bi³⁺ couple is negative shifted at $E_{pa} = -0.085$ V vs. Ag/AgCl, KCl_{sat}.

Pb²⁺ detection at BiCXe-CPE electrode

Commonly, stripping analysis has been used for trace metal analysis. It was considered as a powerful tool because of its remarkable sensitivity which is attributed to the combination of an effective accumulation step and a pulse measurement which generates an extremely great signal-to-background ratio. In the literature was reported that Bi-based electrodes are less susceptible to oxygen interference, exhibiting a lower background current for square wave anodic stripping voltammograms (SWASV) even in an aerated solution.²⁰

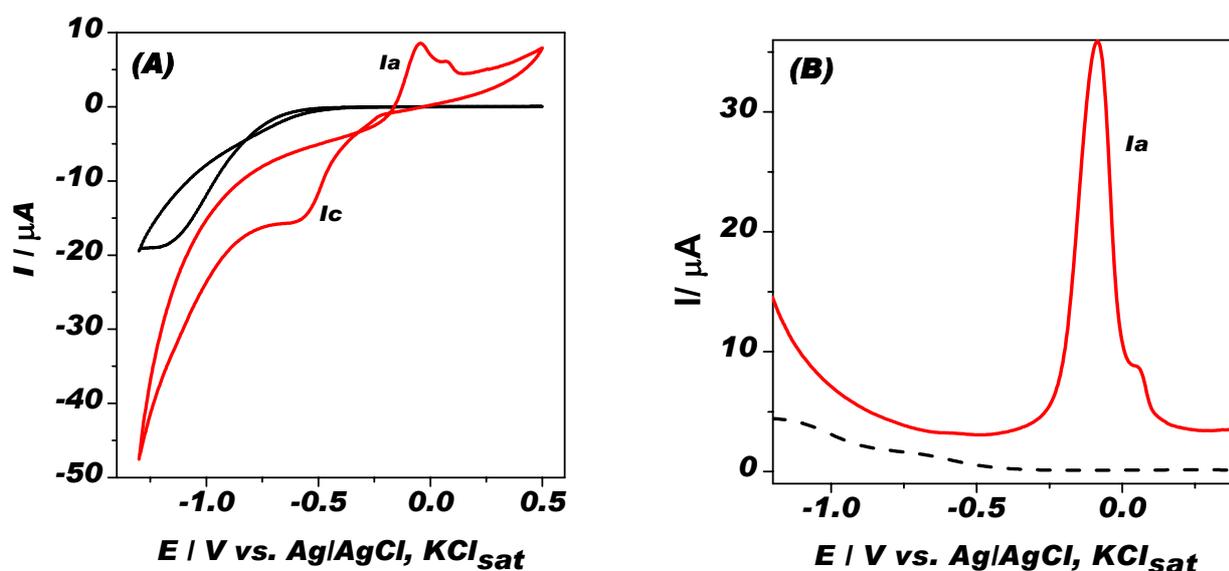


Fig. 3 – CVs (A) and SWASVs (B) at CPE-CXe (dash line) and CPE-BiCXe (solid line). Experimental conditions: electrolyte, 0.1 M acetate buffer (pH 4); starting potential, -1.3 V vs. Ag/AgCl, KCl_{sat}; scan rate, 0.050 V/s; frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.004 V; equilibration time, 10 s.

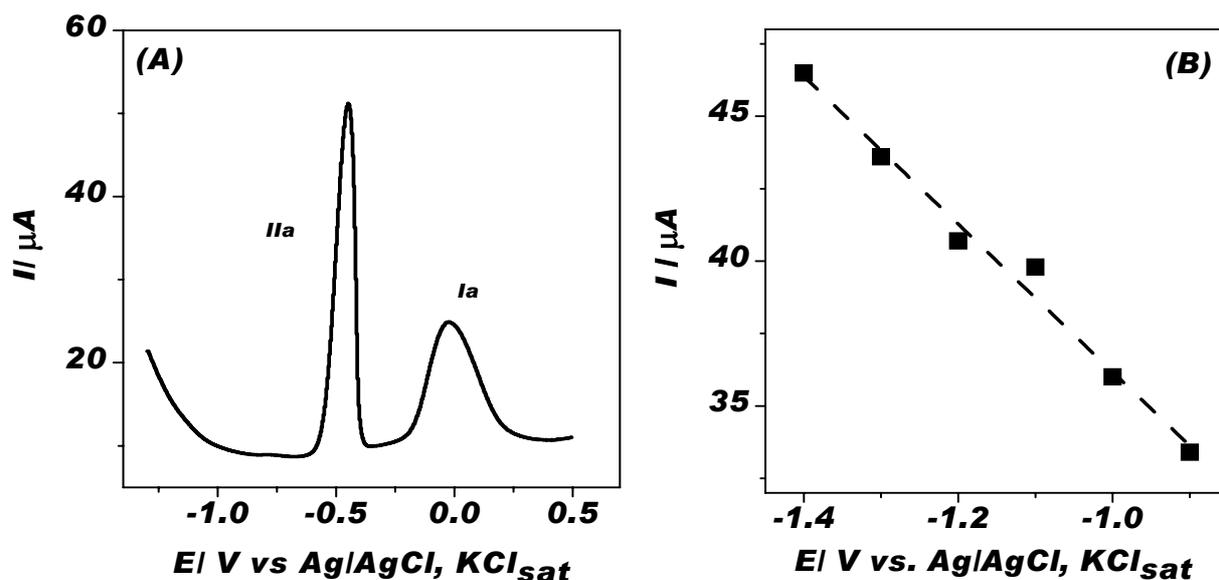


Fig. 4 – SWASV for Pb^{2+} detection at BiCXe-CPE electrode (A) and the influence of the deposition potential on the detection of $2 \mu\text{M}$ Pb^{2+} at BiCXe-CPE electrode by SWASVs (B). Experimental conditions: electrolyte, 0.1 M acetate buffer (pH 4.5); starting potential, $-1.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$; frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.004 V; deposition potential -0.9 to $-1.4 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$; deposition time, 120 s under continuous stirring at 500 rpm; equilibration, 10 s without stirring; electrode conditioning, $+0.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$; duration, 30 s under continuous stirring at 500 rpm.

For Pb^{2+} detection by SWASV a first step of preconcentration was operated at $-1.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$ for 120 s under continuous stirring. A controlled stirring at 500 rpm was used, in view to increase the convective mass transport of the metal ions to the electrode surface.²¹ Then, the stirring was stopped and after a 10 s equilibration period, the voltammogram was recorded by applying a positive-going square-wave stripping voltammetric potential scan as showing in Fig. 4A. The potential of peak IIa attributed to Pb/Pb^{2+} oxidation is placed at $-0.530 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$, value in agreement with those reported in literature for similar electrodes (*i.e.*, -0.6 ÷ $-0.5 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$ at Bi film *in situ* on graphene-carbon paste electrode,²² $-0.5 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$ at Bi-xerogel/Nafion-modified glassy carbon electrode²³ or at Bi bulk electrode).²¹ In view to clean the electrode surface from any remaining traces of metals, after each measurement, a conditioning step consisting in an applied potential of $+0.30 \text{ V}$ during 30 s under stirring at 500 rpm was employed.

In order to obtain the best voltammetric behavior of the BiCXe-CPE for Pb^{2+} detection, several operational parameters of SWASV including deposition time or deposition potential were investigated.

The deposition potential which must be applied in order to reduce easily the metal ions to be

detected should generally be 0.3 – 0.5 V more negative than the oxidation potential of Pb^{2+} .²⁴ Consequently, the effect of the deposition potential on metal stripping signals for the detection of $2 \mu\text{M}$ Pb^{2+} was studied with a deposition time of 120 s under continuous stirring at 500 rpm in the range from -0.9 up to $-1.4 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$. In the acetate buffer, this potential domain avoid the hydrogen evolution which can have an influence on the metal deposited on the electrode surface.¹¹ As expected, the stripping peak currents increase linearly when the deposition potential shifts from -0.9 to $-1.4 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$, as shown in Fig. 4B, following the equation: $I/A = (10.7 \cdot 10^{-6} \pm 1.8 \cdot 10^{-6}) - (25.5 \cdot 10^{-6} \pm 1.53 \cdot 10^{-6}) E_{\text{deposition}}/V$, $R = 0.9929$, $n = 6$. As a high enough peak intensity for Pb^{2+} detection was observed at a deposition potential of $-1.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$, this value was selected for following experiments.^{16,23}

Preconcentration or deposition time is the time during which the Pb^{2+} ions are reduced at the BiCXe-CPE electrode to form the Pb-Bi intermetallic compounds. It is generally accepted that a lower limit of detection can be obtained with longer deposition time.²⁴ Therefore the effect of the deposition time on the stripping peak currents of Pb-Bi intermetallic compounds was studied in the range of 100 s up to 500 s (Fig. 5). As seen in the inset of Fig. 5, a linear dependency of the peak current is obtained at deposition times lower than

200 s, with a slope of 200 nA/s ($R = 0.9989$, $n = 5$) proving a higher selectivity than that at a silver electrode manufactured from a recordable compact disc (ACD), when a slope of 180 nA/s ($R^2 = 0.9978$) was reported.²⁵ At deposition time greater than 200 s, gradual leveling-off at 500 s is observed, probably due to the saturation loading of the electrode surface.^{11,23} Because in routine measurements, the best choice is a compromise between sensitive analysis and reasonable analysis time, an accumulation time of 120 s was chosen as the optimal deposition time.¹¹

The SWAS voltammograms recorded under optimal above established experimental conditions, for different concentrations of Pb^{2+} ions, showed a well-defined peak shape corresponding to the oxidation of $Pb(0)$ accumulated at the surface of BiCXe-CPE (Fig. 6A). The resulting calibration curve has a linear range between $2 \cdot 10^{-9}$ and $5 \cdot 10^{-9}$ M Pb^{2+} , described by the equation $I/A = (1.54 \cdot 10^{-5} \pm 2.19 \cdot 10^{-7}) + (453.06 \pm 59.96) [Pb^{2+}]/M$ ($R = 0.9829$, $n = 6$) (Fig. 6B).

The limit of detection (LOD, estimated for signal/noise ratio of 3) was $0.18 \mu\text{g/l } Pb^{2+}$. This value is smaller than $1.3 \mu\text{g/l } Pb^{2+}$ which was obtained for a similar GC/Bi-xerogel/Nafion electrode.²³ It is

interesting to point out that for higher concentration range of Pb^{2+} (Table 1) the relative high detection limit can be explained by the (i) the random distribution of the Bi in the electrode matrix and (ii) by the lower conductivity of the relatively small amount of BiCXe than that of the graphite substrate in the composite electrode matrix.²⁶

One of the most important performance characteristic of a sensor is its reproducibility, expressed as relative standard deviation (RSD) of the peak current. Thus, for 3 consecutive experiments with the same BiCXe-CPE electrode surface, the mean peak intensity is $4.86 \cdot 10^{-5} \pm 0.019 \cdot 10^{-5}$ A for $2 \mu\text{M } Pb^{2+}$ with a RSD of 0.39%. The satisfactory values of recovery show that the developed sensor is suitable for lead determination in real samples of water at levels relevant for regulatory purposes.¹⁴

Moreover, the analytical parameters of BiCXe-CPE are satisfactory when compared with the maximum admissible concentration of $10 \mu\text{g } Pb^{2+}/\text{l}$ required by the UE legislation for the drinking water,²⁷ as consequence the device can be used for application in real samples.²⁶

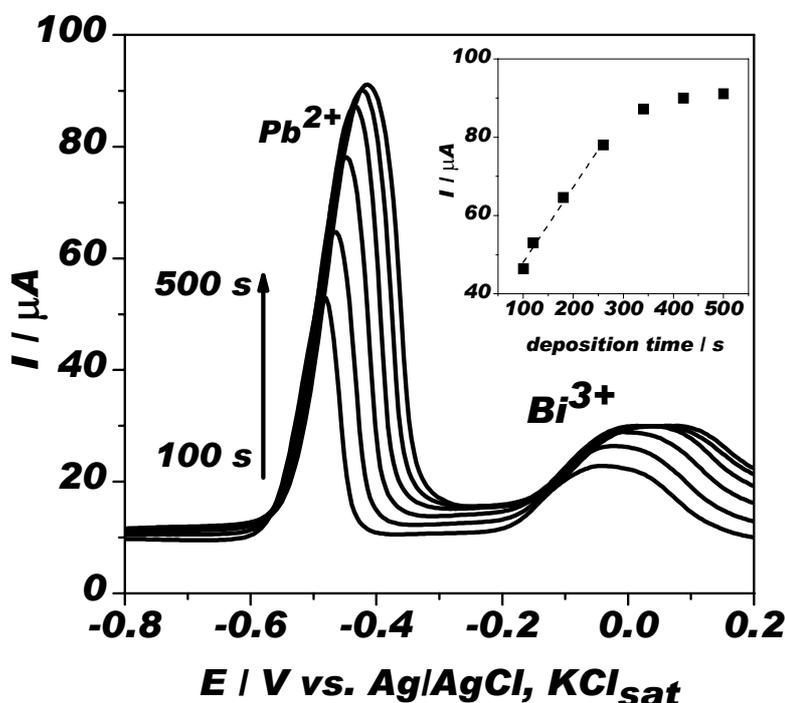


Fig. 5 – The influence of the deposition time on the detection of $2 \mu\text{M } Pb^{2+}$ at BiCXe-CPE electrode by SWASV. Inset: Dependency of Pb^{2+} peak current intensity vs. deposition time. Experimental conditions: electrolyte, 0.1 M acetate buffer (pH 4.5); starting potential, $-1.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$; frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.004 V; deposition potential $-1.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$; deposition time, 100 s to 500 s under continuous stirring at 500 rpm; equilibration, 10 s without stirring; electrode conditioning, $+0.3 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$; duration, 20 s under continuous stirring at 500 rpm.

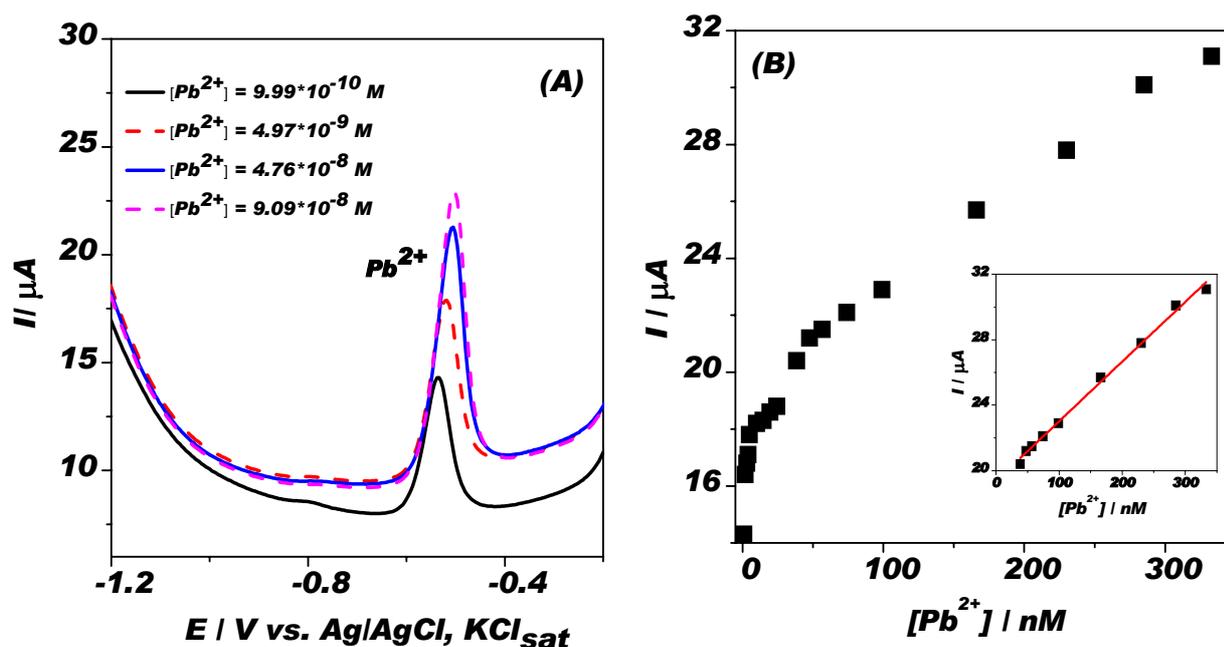


Fig. 6 – SWASVs for Pb²⁺ determination at the BiCXe-CPE electrode (A) and the corresponding calibration curve (B). Experimental conditions: electrolyte, 0.1 M acetate buffer (pH 4); starting potential, -1.3 V vs. Ag/AgCl, KCl_{sat}; frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.004 V; deposition potential -1.3 V vs. Ag/AgCl, KCl_{sat}; deposition time, 120 s under continuous stirring at 500 rpm; equilibration, 10 s without stirring; electrode conditioning, +0.3 V vs. Ag/AgCl, KCl_{sat}; duration, 20 s under continuous stirring at 500 rpm.

Table 1

Analytical parameters for the detection of Pb²⁺ ions at BiCXe-CPE. Experimental conditions: see Fig. 4

Linear range M	Sensitivity A/M	LOD M	LOD μg/L	SD	R/n
2 · 10 ⁻⁹ ÷ 5 · 10 ⁻⁹	453.06 ± 59.96	8.81 · 10 ⁻¹⁰	0.18	1.33 · 10 ⁻⁷	0.9829 /6
5 · 10 ⁻⁹ ÷ 2.5 · 10 ⁻⁸	49.66 ± 4.63	4.28 · 10 ⁻⁹	0.88	7.09 · 10 ⁻⁸	0.9872 /5
2.5 · 10 ⁻⁸ ÷ 3.5 · 10 ⁻⁷	37.95 ± 1.56	4.12 · 10 ⁻⁸	8.55	5.22 · 10 ⁻⁷	0.9933/10

* LOD calculated as 3*SD/slope of the equation $I/A = a + b [Pb^{2+}]/M$.

Determination of Pb²⁺ in the presence of Cd²⁺

The toxic heavy metal ions Cd²⁺ and Pb²⁺ may simultaneously exist in real samples, their detection being necessary in these conditions. Moreover, it is well-known that the presence of the Bi on the BiCXe-CPE electrode surface can cause different forms of Cd–Bi and Pb–Bi intermetallic compounds during the accumulation step, which suffer dissociation at different potential values during the stripping step.²² Consequently the determination of Pb²⁺ in the presence of Cd²⁺ ions on the BiCXe-CPE was investigated by SWASV, under the optimal conditions determined for the individual detection of ions.^{11,16,21,22} The voltammograms obtained in a solution containing the same concentrations of Cd²⁺ and Pb²⁺ ions are shown in Fig. 7A. The anodic peak currents of both metal ions exhibited well-defined peaks

placed at -0.8 V vs. Ag/AgCl, KCl_{sat} and -0.54 V vs. Ag/AgCl, KCl_{sat}, for Cd/Cd²⁺ and Pb/Pb²⁺ oxidation, respectively.

From the calibration curves for the Cd²⁺ and Pb²⁺ ions mixture (Fig. 7B) the calculated sensitivities are: 9.36 ± 1.13 A/M for Cd²⁺ (R = 0.9789, n = 5) and 17.31 ± 1.68 A/M for Pb²⁺ (R = 0.9861, n = 5). The Cd(0) accumulated on the electrode surface are stripped off before Pb(0), and in the process of stripping, are also removing a significant portion of the accumulated Pb(0), as well, causing a 54% relative decrease in sensitivity for Pb²⁺.²¹

This BiCXe-CPE electrode has been found sufficiently selective over the Pb²⁺ ions, so it can be applied not only to individual determination of Cd²⁺,²⁸ but also to the simultaneous determination of Cd²⁺ and Pb²⁺.¹⁶

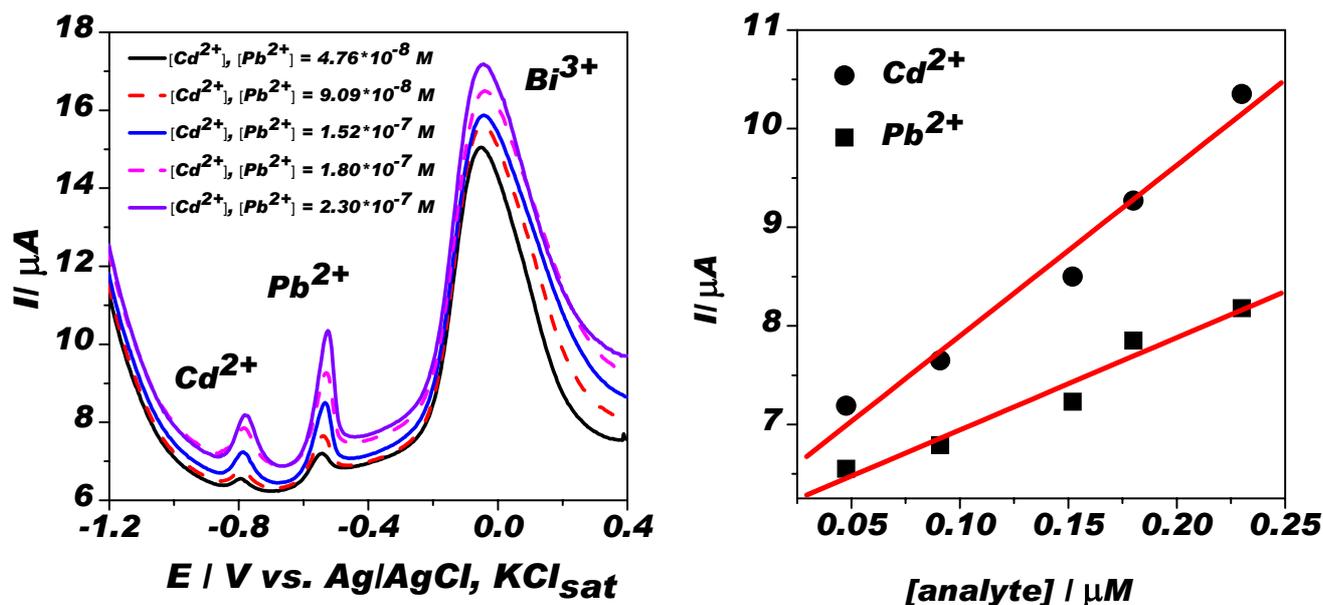


Fig. 7 – SWASVs responses for increasing concentrations of Cd^{2+} and Pb^{2+} (A) and the corresponding calibration curves (B) at BiCXe-CPE electrode. Experimental conditions: starting potential, -1.3 V vs. Ag/AgCl, KCl_{sat} ; deposition time 120 s under continuous stirring; other conditions see Fig. 3.

CONCLUSIONS

The Bi-modified electrode (BiCXe-CPE) is less toxic than mercury electrodes and has the advantages of being simple, cost effective and independent of the dissolved oxygen present in the working solutions. Stripping analysis coupled to BiCXe-CPE modified electrodes lead to wide linear dynamic range and a low detection limit ($0.18 \mu\text{g L}^{-1} \text{Pb}^{2+}$). Other advantages are easy handling and modification, low toxicity and low cost, which recommend them for the trace analysis of Pb^{2+} and Cd^{2+} .

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REFERENCES

- World Health Organization, Guidelines for drinking water Quality, 3rd edition, World Health Organization (WHO) Geneva, 2008.
- T.R. Copeland and R.K. Skogerboe, *Anal. Chem.*, **1974**, *46*, 1257A-1268A.
- W.D. Ellis, *J. Chem. Educ.*, **1973**, *50*, A131.
- J. Wang, *Electroanalysis*, **2005**, *17*, 1341-1346.
- Kirk Othmer, “Encyclopedia of chemical technology”, John Wiley & Sons, New York, 1978, vol. 3, p. 912-937.
- H. Xu, L. Zeng, D. Huang, Y. Xian and L. Jin, *Food Chem.*, **2008**, *109*, 834-839.
- A. Charalambous and A. Economou, *Analyt. Chim. Acta*, **2005**, *547*, 53-58.
- C. Kokkinos, A. Economou, I. Raptis and C.E. Efstathiou, *Electrochim. Acta*, **2008**, *53*, 5294-5299.
- H. Li, J. Li, Zh. Yang, Q. Xu, Ch. Hou, J. Peng and X. Hu, *J. Hazardous Mat.*, **2011**, *191*, 26-31.
- L. Zhu, B. Huang, N. Jia, L. Tan and S. Yao, *Electrochim. Acta*, **2014**, *115*, 471-477.
- D. Li, J. Jia and J. Wang, *Talanta*, **2010**, *83*, 332-336.
- G. Aragay, *Electrochim. Acta*, **2012**, *84*, 49-61.
- I. Svancara, C. Prior, S. B. Hocevar and J. Wang, *Electroanalysis*, **2010**, *22*, 1405-1420.
- J.C. Quintana, F. Arduini, A. Amine, F. Punzo, G. Li Destri, C. Bianchini, D. Zane, A. Curulli, G. Palleschi and D. Moscone, *Anal. Chim. Acta*, **2011**, *707*, 171-177.
- K.E. Toghill, G.G. Wildgose, A. Moshar, C. Mulcahy and R.G. Compton, *Electroanalysis*, **2008**, *20*, 1731-1737.
- J.H. Luo, X.X. Jiao, N.B. Li and H.Q. Luo, *J. Electroanal. Chem.*, **2013**, *689*, 130-134.
- M. Gich, C. Fernandez-Sanchez, L.C. Cotet, P.F. Niu and A. Roige, *J. Mater. Chem. A*, **2013**, *1*, 11410-11418.
- C.I. Fort, L.C. Cotet, V. Danciu, G.L. Turdean and I.C. Popescu, *Mater. Chem. Phys.*, **2013**, *138*, 893-898.
- E. Laviron, L. Roullier and R. Gavasso, *J. Electroanal. Chem.*, **1979**, *101*, 19-28.
- G.J. Lee, H.M. Lee and C.K. Rhee, *Electrochem. Commun.*, **2007**, *9*, 2514-2518.
- K.C. Armstrong, C.E. Tatum, R.N. Dansby-Sparks, J.Q. Chambers and Z.L. Xue, *Talanta*, **2010**, *82*, 675-680.

22. W. Wonsawat, S. Chuanuwatanakul, W. Dungchai, E. Punrat, S. Motomizu and O. Chailapakul, *Talanta*, **2012**, *100*, 282-289.
23. P.A. Dimovasilis and M.I. Prodromidis, *Anal. Chim. Acta*, **2013**, *769*, 49-55.
24. C. Elliott and D. Rutledge, *Trends Anal. Chem.*, **2010**, *29*, 1237-1238.
25. K.C. Honeychurch, *Adv. Anal. Chem.*, **2013**, *3A*, 28-33.
26. Z. Zou, A. Jang, E. Macknight, P.M. Wu, J. Do, P.L. Bishop and C.H. Ahn, *Sens. Actuators B*, **2008**, *134*, 18-24.
27. *** Council Directive 98/83/CEE of 3 November 1998 relating to the quality of water intended for human consumption, *Official Journal* no. 330/32 of 05.12.1998, p. 11.
28. A.R. Deac, L.C. Cotet, G.L. Turdean and L.M. Muresan, *Studia Univ. Babeş Bolyai Chem.*, **2015**, *60*, 203-212.

