



Ca₁₀(PO₄)₆(OH)₂-modified carbon-paste electrode for the determination of trace lead(II) by square-wave voltammetry

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ABSTRACT

The analytical performance of hydroxyapatite Ca₁₀(PO₄)₆(OH)₂(HAp) screen-printed sensors designed for the detection of metals was evaluated. The hydroxyapatite plays an important role in modern analytical electrochemistry due to their usefulness for the preparation of sensors giving rise to improved responses from metals. The suitable HAp-modified carbon-paste electrode (HAp-CPE) for the electrochemical determination of lead is illustrated in this work using cyclic and square-wave voltammetry in the potential range between −0.3 and −0.8 V. Perchlorate acid solution (1.0 mol L^{−1}) was employed as the supporting electrolyte. The voltammetric measurements were carried out using as working electrode HAp-CPE, and a platinum electrode and an SCE electrode as auxiliary and reference electrodes, respectively. Under the optimized working conditions, calibration graph is linear for 5 min of preconcentration time with the detection limit 7.68 × 10^{−10} mol L^{−1}. This detection limit is remarkably lower than those reported previously using other modified electrodes or amperometric detection. The results indicate that this electrode is sensitive and effective for the determination of Pb²⁺.

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1. Introduction

Environmental monitoring of heavy metals is of great importance for ecological assessments as well as for understanding the dissemination of pollutants [1]. Contamination by metals is indeed widespread all over the world [2]. Pollution with lead is a highly significant risk factor in predicting higher rates of crime, attention deficit disorder or hyperactivity, and learning disabilities. Exposure and uptake of lead has been associated with industrial pollution, leaded paint and plumbing systems in old housing, lead residues in soil. Detection of toxic trace lead in the environment is a challenging analytical problem. The major existing techniques for metal trace analyses are spectroscopic (in particular, graphite furnace atomic adsorption spectroscopy (GF-AAS) and inductively coupled plasma mass spectroscopy (ICP-MS)), voltammetric and chronoamperometric. Recently, it has been demonstrated that the chemically modified carbon-paste electrodes (CMCPes) have received considerable attention due to their numerous advantages, such as easy manufacture, no poison, low price, wider operational window, renewable surface, stability in various solvents and longer life time [3,4]. For trace determination, use of an Hg-film electrode has been shown to be necessary to achieve sub-μg L^{−1} detection limits

for complex environmental samples [5]. Because Hg is toxic, however, its incorporation into sensors poses problems, particularly with regard to disposability [6]. It has made necessary to develop a sensitive and non-toxic electrode for the determination of heavy metals. For example, bismuth-film electrodes have been shown to offer comparable performance to mercury electrode in anodic stripping voltammetry [7–11]. It has been shown that bismuth-film electrodes maintain all the advantages of mercury electrodes and, at the same time, are environmentally friendly as the toxicity of bismuth and its salts is negligible. In addition to their lower toxicity, bismuth-film electrodes resulted in compared to the performance of mercury electrodes were less sensitive to dissolved oxygen and had a wide potential window for analysis. However, the determination of copper using bismuth-film electrodes has been relatively ignored due to the similar stripping potentials of copper and bismuth with only a few reports in the open literature [12,13].

Hydroxyapatite-modified platinum was recently used for the determination of lead with a detection limit of 5 × 10^{−7} mol L^{−1} [14], the analytical performances of the method and the apatite–lead interaction were investigated using, cyclic voltammetry, differential pulse voltammetry, energy dispersive analysis of X-ray and electrochemical impedance spectroscopy.

The incorporation of specially chosen modifiers in the electrodes for collection of the analytes prior to voltammetric analysis gives rise to high selectivity and sensitivity. In the past, several kinds of

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modifiers carbon-paste electrodes have been used for lead determination [18–21].

During the past 6 years, our group have studied the use of phosphate compounds [15] to promote organic transformation [16] and have shown that its mild basic and acidic properties can be exploited in many synthetic applications [17].

In this work we prepared and characterized the hydroxyapatite-modified carbon-paste electrode, which successfully exploits the favorable mechanical and electrochemical properties of carbon-paste electrodes. The high flexibility of apatite structures $\text{Ca}_5(\text{PO}_4)_3(\text{OH})_2$ with Ca can be replaced by a number of bivalent cations Sr^{2+} , Ba^{2+} , Cd^{2+} , Pb^{2+} , but monovalent and trivalent cations, such as Na^+ , K^+ and Al^{3+} can be hosted as well; PO_4 is usually VO_4^{3-} or AsO_4^{3-} , but the possible substitutions include also SiO_4^{4-} , CO_3^{2-} and SO_4^{2-} ; OH^- is a monovalent anion F^- , Cl^- , Br^- [22–25]. The great variety of cationic and anionic substitutions is justified by the “open structure” of apatite. Our work develops the electrochemical technology of the trapping of the mineral micropollutants in solution such as lead using the synthesis apatite. Once lead comes in touch with the HAp-modified carbon paste, it is rapidly and strongly fixed to apatite. Its remarkable sensitivity is due to fixation step, during which the analyte lead was accumulated on the working electrode. This method is relatively inexpensive when compared to the spectroscopic techniques, and the feasibility of compact portable instruments makes it attractive for field on-line monitoring of trace metals [26–29].

2. Experimental

2.1. Reagent

$\text{Pb}(\text{NO}_3)_2$ was dissolved into Bi-distilled deionized water (BDW) to form $10^{-3} \text{ mol L}^{-1}$ stock solutions. Working standards for calibration were prepared by diluting the primary stock solution with BDW. Carbon paste was supplied from (Carbone, Lorraine, ref. 9900, French). All chemicals were of analytical grade and used without further purification.

2.2. Hydroxyapatite preparation

The hydroxyapatite used in this manuscript was synthesized with the double decomposition method [30] in aqueous medium using stoichiometric quantities of ammonium hydrogen phosphate (solution A) and calcium nitrate (solution B). Solution A was prepared by adding ammoniacal solution (200 mL) to an aqueous solution of $(\text{NH}_4)_2\text{HPO}_4$ (7.92 g in 800 mL). Solution B was obtained by dissolving $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in bidistilled water (23.6 g in 400 mL) and then is added drop by drop into a boiling diammonium phosphate solution containing NH_4OH . The solution was heated at 90°C . The precipitate was maintained in contact with the reaction solution for 5 h at 90°C under stirring, and repeatedly washed with distilled water. The product was dried at 100°C over night.

2.3. Instrumentation and software

Square-wave voltammetry was performed with a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software) connected to Pentium III computer run under Windows 98. The electrochemical cell contains a HAp-modified carbon paste working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE).

The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

An evaluation of the purity of the hydroxyapatite powder was carried out by The X-ray diffraction analysis (XRD: Cu $\text{K}\alpha$ radiation, XPERT) produced at 30 kV and 25 mA scanned the diffraction angles (2θ) between 10 and 70 with a step size of 0.02, 2θ per second. The volume V of the hexagonal unit cell was determined for each HAp formulation from the relation $V = a^2c \sin 2\pi/3$. Crystallographic identification of the phases of synthesized apatite was accomplished by comparing the experimental XRD patterns to standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS), namely the following card numbers: *09-0432* for HAp [31]. Fourier transformed infrared spectroscopy (FTIR) analysis (PerkinElmer FTIR) was performed in order to determine hydroxyapatite stoichiometry deviations, in particular the PO_4^{3-} and/or OH^- groups. In order to evaluate Ca/P ratio of the powder, inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer DV 3300) analysis was performed.

2.4. Preparation of HAp-CPE

HAp-modified carbon-paste electrode was prepared according the following procedure [15]. The modified carbon-paste electrode was prepared by mixing the graphite powder with the HAp to give an appropriate ratio HAp/CP. The mixture was grinding in a mortar agate and then a portion of the resulting composite material was housed in PTFE cylinder. The geometric surface area of the working electrode was 0.1256 cm^2 . A bare of carbon vitreous inserted into carbon paste provided the electrical contact.

2.5. Procedure of voltammetric measurements

For the electroanalytical determination of the concentration of lead in aqueous samples, a two-step procedure was followed. The electrode was first immersed in a preconcentration solution containing the target analyte at a given concentration and selected pH. Where the accumulation of lead species was achieved chemically by binding to HAp at open circuit, the HAp-CPE was then removed from the accumulation cell, rinsed with BDW, and transferred to separate voltammetric cell containing only a supporting electrolyte ($0.1 \text{ mol L}^{-1} \text{ HClO}_4$). For experiments voltammetry the potential range was from -0.3 to -0.8 V and scan rate was 50 mV s^{-1} . All measurements were carried out at room temperature.

The square-wave voltammograms were recorded in different lead concentrations using 5 mV of the pulse amplitude, step potential 25 mV and the duration time is 5 s at scan rate 1 mV s^{-1} .

According to Miller and Miller [32] the standard deviation of the mean current σ measured at oxidation potential of lead was calculated for five voltammograms of the blank solution. The calculated σ was used in the determination of the detection limit (DL, $3\sigma/\text{slope}$) and the quantification limit (QL, $10\sigma/\text{slope}$).

The suitability of the electroanalytical working procedure in detecting lead in natural matrices was tested by spiking tap and domestic water samples. After contamination, the same electroanalytical procedure described for the pure electrolyte was applied in the tap and domestic water samples.

3. Results and discussion

3.1. Synthesized powders

The XRD pattern of the synthesized powder reveals an apatite structure. The crystallographic lattice parameters calculated using the AF-part program were $a = 9426 \text{ \AA}$, $c = 6887 \text{ \AA}$ and $V = 52,917 \text{ \AA}^3$. A FT-IR pattern also coincides with the results from XRD. FT-IR spectra for the as dried powder have indicated the vibration modes of PO_4 groups at 475, 574, 609, 966 and $1020\text{--}1120 \text{ cm}^{-1}$ and OH

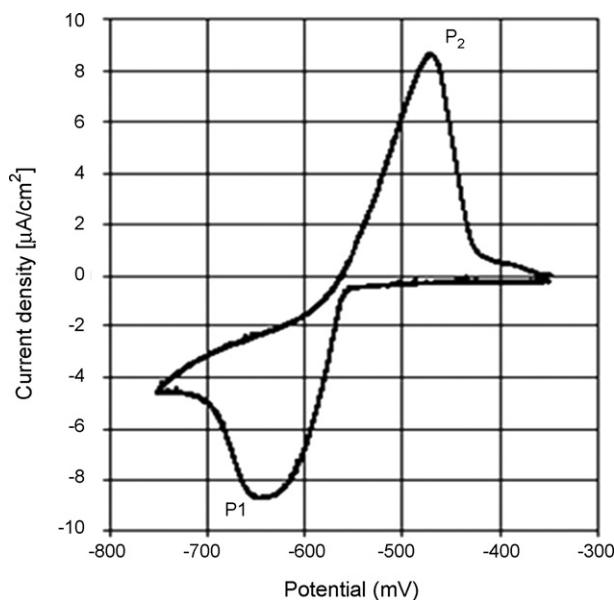


Fig. 1. Cyclic voltammogram of $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb}^{2+}$ in $1.0 \text{ mol L}^{-1} \text{ HClO}_4$, 5 min of preconcentration time (tp), pH 8.0, scan rate, 50 mV s^{-1} at HAp-CPE (4% HAp).

groups (630 and 3570 cm^{-1}) of apatite powder [33]. Portions of calcium and phosphorus of the synthesized hydroxyapatite were obtained using ICP. The calcined HAP has following chemical composition: Ca (35.115%), P (16.171%), which are in agreement with the stoichiometric values of HAP.

3.2. Voltammetric characterization

In order to avoid the strong residual current of reduction, the starting potential was fixed at -0.8 V versus SCE. Fig. 1 shows a cyclic voltammogram performed between -0.3 and -0.8 V for 4% HAp-modified carbon-paste electrode, obtained after exposure to $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb}^{2+}$ for 5 min in a stirred solution. The reversible system could be observed with a cathodic value E_c of -0.63 V and an anodic value E_a of -0.49 V .

The influence of scan rate was studied with HAp-CPE immersed for 5 min in $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb}^{2+}$. The oxidation peak was found to vary linearly with the scan rate ranging from 10 to 200 mV s^{-1} (Fig. 2). Pb^{2+} ions diffused from the preconcentration solution towards the interstitial space existing in the paste electrode modified with HAP. The application of -0.8 V leads to a lead-reduction that coated graphite particles. Then, the dissolution process by

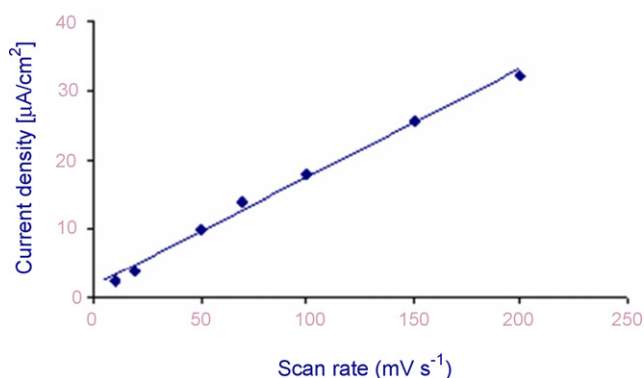


Fig. 2. Influence of the scan rate on the oxidation peak intensity for $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb}^{2+}$ (pH 8.0) in $1.0 \text{ mol L}^{-1} \text{ HClO}_4$, preconcentration time: 5 min.

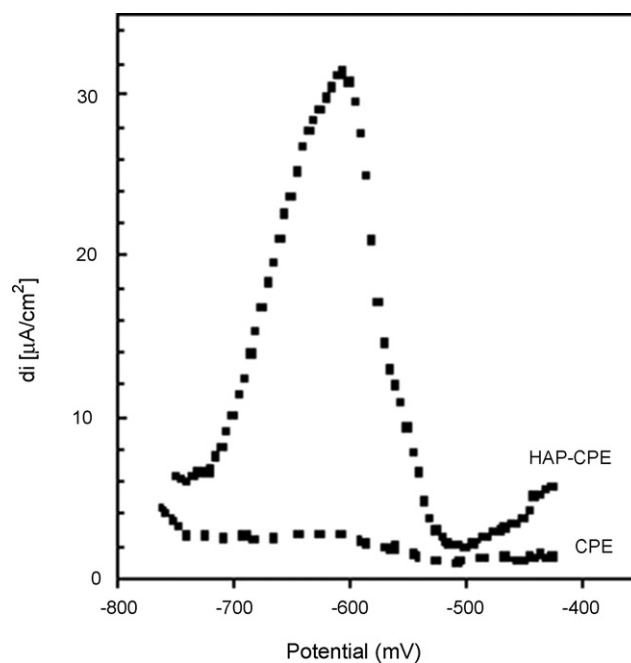


Fig. 3. Square-wave voltammograms of $4.3 \times 10^{-6} \text{ mol L}^{-1}$ of lead (pH 7.0) in $1.0 \text{ mol L}^{-1} \text{ HClO}_4$ at different carbon-paste electrodes: (a) HAp-modified carbon-paste electrode; (b) carbon-paste electrode, accumulation time: 5 min; 4% of HAp/CP ratio.

positive scan was quite similar to the redissolution of metal deposit.

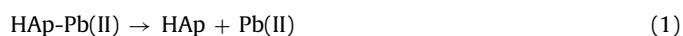
The performance of the newly developed HAp-modified carbon-paste electrode is based on the preconcentration of Pb^{2+} from aqueous solution onto the surface of the modified electrode. As can be seen from Fig. 3, the peak current of lead at the HAp-modified electrode is intense than that of unmodified electrode. Thus there is a substantial enhancement in lead oxidation peak current when HAp-modified electrode is used. This fact is in accordance with the aforementioned experiences in which compounds such as HAP has been successfully used to immobilize the lead from solution media.

3.3. Optimization parameter

To optimize the performance of the HAp chemically modified carbon-paste electrode, for the electrochemical determination of lead in aqueous solution, we investigated the parameters influencing the response of Pb^{2+} , including the electrolyte support, preconcentration time, HAP loading and pH of accumulation solutions.

Pb^{2+} ions have different electrochemical behaviors in different electrolytes. The effects of some electrolytes, such as HCl, HNO_3 and HClO_4 , on oxidation of peak currents of Pb^{2+} were studied. The results show that Pb^{2+} ions have the best electrochemical responses in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$. When the measurements were performed in this electrolyte, the lowest background current and the best shape of peak were obtained.

An acidic medium was selected as suitable for relegate of Pb according to Eq. (1). Pb^{2+} species leached out from the HAP at the electrode/solution interface can be detected directly by reduction Eq. (2):



The influence of pH on the determination of lead was also investigated (Fig. 4). As the pH increased from pH 3.0 to 8.0, the peak

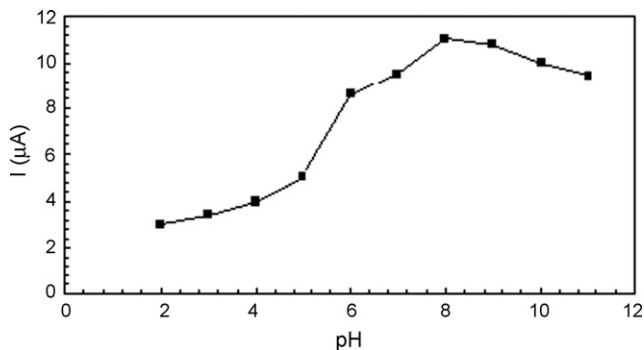


Fig. 4. Effect of the pH on SWV peak height of $1.35 \times 10^{-7} \text{ mol L}^{-1}$ lead in 1.0 mol L^{-1} HClO_4 , HAp/CP=4%, $t_p=7 \text{ min}$.

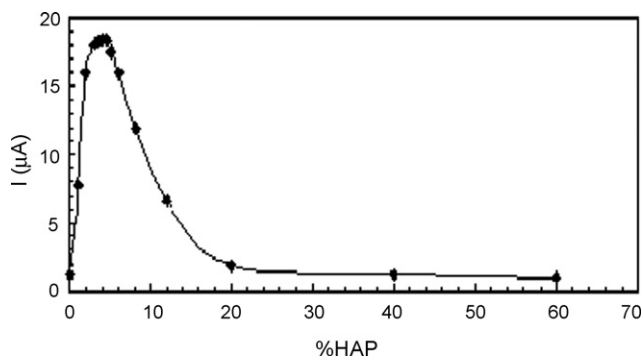


Fig. 5. Influence of the content of HAp in carbon-paste mixture % (w/w) on SWV peak currents of $2.3 \times 10^{-7} \text{ mol L}^{-1}$ lead in 1.0 mol L^{-1} HClO_4 , $t_p=7 \text{ min}$, pH 8.0.

current increased at first because HAp can slowly dissolve in acidic solution and lose its ability of immobilizing Pb^{2+} ions. Then the peak current reached a maximum value around pH 8.0.

The effect of the carbon paste composition in the voltammetric response of the electrode modified with HAp was evaluated by square-wave voltammetry of $2.3 \times 10^{-7} \text{ mol L}^{-1}$ $\text{Pb}(\text{II})$ in 0.10 mol L^{-1} perchlorate acidic media (Fig. 5). The anodic peak current increased with the amount of apatite in the paste up to 4% (w/w). Beyond the anodic peak current decreased significantly, this probably occurs due to a decrease in the conductive area at the electrode surface. According by these results a carbon-paste composition of 4% (w/w) by weights was used in further experiments.

The investigation of the effect of the accumulation time (varied from 0 to 40 min) on the square-wave voltammetric peak current intensities as shown in Fig. 6 was made with $2 \times 10^{-7} \text{ mol L}^{-1}$ of $\text{Pb}(\text{II})$. As expected, the peak current increases with increasing accu-

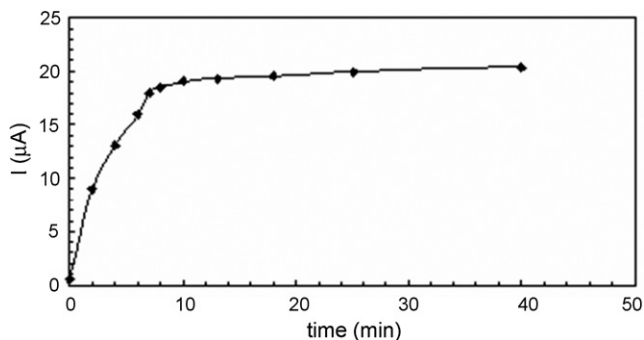


Fig. 6. Influence of preconcentration time on the peak intensity of $2 \times 10^{-7} \text{ mol L}^{-1}$ lead (pH 7.0) on SWV at HAp-CPE in 1.0 mol L^{-1} HClO_4 with 4% of HAp/CP ratio.

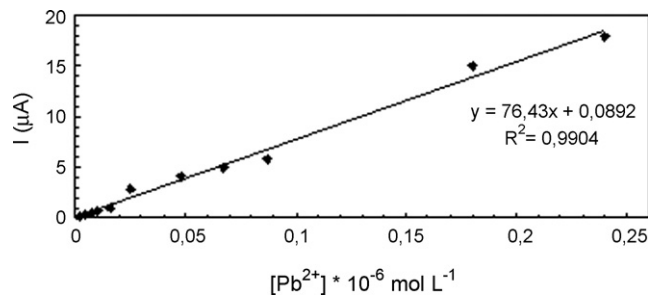


Fig. 7. Influence of concentration of lead on the peaks intensity at HAp-CPE under the optimized conditions.

mulation time; however, a plateau was reached after 7 min. Thus, this interval time as accumulation time was chosen as a good compromise between length of analysis, sensitivity and reproducibility.

3.4. Calibration plots

The concentration range from 2×10^{-9} to $2.4 \times 10^{-7} \text{ mol L}^{-1}$ was examined for proportionality of the HAp-CPE signal with concentration of lead by analyzing model solutions containing appropriate additions of $\text{Pb}(\text{II})$. The linear calibration plots (Fig. 7) were obtained under optimal conditions. The regression straight line has the following equation $i_{\text{P}2} = 76.43 [\text{Pb}] + 0.0892$, where $i_{\text{P}2}$ is expressed in μA and the concentration in $\mu\text{mol L}^{-1}$ and the correlation coefficient was 0.9904.

The observed values of DL and QL for peak 2 were $7.68 \times 10^{-10} \text{ mol L}^{-1}$ and $2.56 \times 10^{-9} \text{ mol L}^{-1}$, respectively. The precision, expressed as relative standard deviation, was 4.1% for five repetitions of $3.5 \times 10^{-7} \text{ mol L}^{-1}$ lead.

From close analysis of the results obtained for DL and QL it is apparent that use of HAp-modified carbon-paste electrodes provides an alternative new method for electrochemical determination of lead, substituting traditional mercury electrodes, which have the inconvenience of being highly toxic. It should, however, be pointed out that although DL and QL obtained in this present study are comparable to the values obtained in the literature [34,35]. Such results are shown to be very appropriate for the determination of ultra-traces of lead in water samples, where the recommended maximum residue stipulated is $25 \mu\text{g/kg}$ [36].

3.5. Fixation mode of lead in the modified paste

On other hand the interest method was tested to understand the entry of $\text{Pb}(\text{II})$ ions into HAp-carbon paste [37]. Since the solubility of lead perchlorate was very large, precipitation of the salts was impossible; 499.7 g of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ may be dissolved in 100 cm^3 of water at 25°C [38]. So adsorption of Pb^{2+} ions on carbon was tested with a suspension of carbon particles vigorously stirred in $10^{-3} \text{ mol L}^{-1}$ lead solution for 70 min by measuring the lead concentration, before and after this adsorption test, by ICP-AES, it was found that no adsorption occurred. So the only preconcentration mode of lead was a concurrence between the adsorption onto apatite surface or/and incorporation into structure and a diffusion from the bulk towards the paste where the interstitial liquid played the role of a captive solution.

To better know the mechanism of fixing lead at HAp-CPE, an electrode containing 100% of HAp has been immersed in a solution of $5 \times 10^{-6} \text{ mol L}^{-1}$ lead for 10 min. Impedance diagrams were plotted in to obtain more details on the mechanism of immobilization of lead onto HAp. The Nyquist plot obtained showed a semicircle corresponding to a charge transfer phenomenon between HAp and solution containing Pb^{2+} ions.

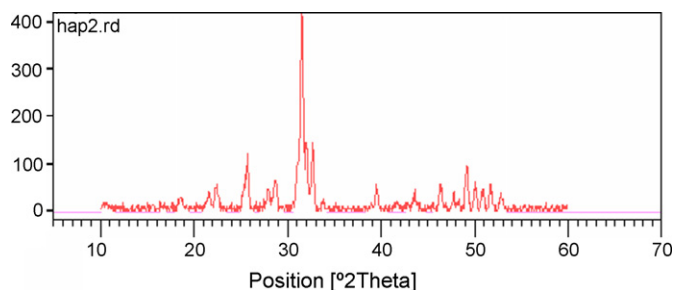
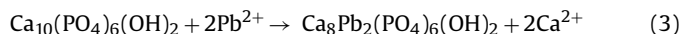


Fig. 8. XRD patterns of hydroxyapatite pre-concentrated in $5 \times 10^{-6} \text{ mol L}^{-1}$ Pb^{2+} solution for 10 min and heated at 900°C for 3 h.

According to Sandrine et al. [39] the mechanism of the reaction between lead ions and the powder of hydroxyapatite corresponds to an equimolar exchange of lead and the calcium to give $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$ matrices, with x can vary from 0 to 10, this substitution depends on reaction times and the experimental conditions. The proposed mechanism of lead fixation by the HAp consists of two stages: first, a fast complexation of lead onto the surface in the sites $\equiv\text{POH}$ of apatite that causes a reduction of pH and secondly, a partial dissolution of the calcium followed by the precipitation of apatite of formula $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$.

Mavropoulos et al. [40] postulate that $\equiv\text{POH}$ sites have been transformed to $\equiv\text{POPb}^+$. The latter lead to decrease the initial pH by liberation of protons H^+ and therefore conducted to the dissolution of the calcium. The progression of the pH toward its initial value depends on the lead concentration; with a concentrated solution the response is slower [39].

The HAp paste obtained after 7 min of accumulation in lead solution has been washed with BDW and calcined at 900°C for 3 h. The identification by X-ray diffraction provides a system of stripes attributable to the hydroxyapatite substituted by lead $\text{Ca}_8\text{Pb}_2(\text{PO}_4)_6(\text{OH})_2$ (Fig. 8):



This result is also confirmed by the chemical analysis (ICP-AES) of calcium and lead. We noticed that the accumulation of lead towards the carbon-paste electrode modified with the hydroxyapatite is limited by the substitution in the site of the calcium and the diffusion toward the interstitial liquid played the role of a capacitive solution.

3.6. Interference studies

We tested the elements that can present a certain competition to the level of the sites on HAp-CPE. This test has been used under the conditions optimized for the determination of the Pb^{2+} ions.

The voltammogramme has been recorded after the preconcentration of HAp-CPE in aqueous solutions of the nitrate of lead, cadmium and copper (Fig. 9). The anodic oxidation of the cadmium occurs to the potential of -0.8 V/SCE , lower to the potential oxidation of lead -0.53 V/SCE . The oxidation peak of copper appears at a potential $+0.021 \text{ V/SCE}$ superior to the potential oxidation of lead. The clean separation of the three potential peaks offers us the possibility of the simultaneous determination of lead, cadmium and copper.

Intensity of the current density of $1 \times 10^{-7} \text{ mol L}^{-1}$ cadmium has been affected by the presence of $1.2 \times 10^{-7} \text{ mol L}^{-1}$ lead and $1.6 \times 10^{-7} \text{ mol L}^{-1}$ copper. It is explained by the capacity of adsorption of HAp that varies according to the scale of affinity decreasing: $\text{Pb} > \text{Cd} > \text{Cu}$. The application of the reduction potential (-1.0 V/SCE) before the voltammetric measurements can also lead to the substitutions in cationic sites of HAp. The substitution of the calcium can

Table 1
Result of Pb^{2+} analysis in tap water samples under the optimized conditions

Element	Added ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$)	Recovery (%)
Pb^{2+}	0.01	0.0089	89
	0.02	0.0188	94
	0.03	0.0303	101
	0.04	0.0424	106

reach 20–30% by Pb^{2+} and 40% by Cu^{2+} , this percentage has been explained in terms of the difference of the ionic ray by Bruckner [41]. The domain of application of HAp-modified carbon-paste electrode is large. This electrode permits to determine some metallic ions simultaneously, which is not the case with other electrode.

3.7. Practical application of this electroanalytical methodology

The presence of other species in the preconcentration solution can affect the analytic results. Because of this, the HAp-CPE has been valued for the determination of traces of lead in tap and domestic waters.

3.8. In tap water

The HAp-CPE was tested in tap water samples under the optimized conditions (Fig. 10). For every sample, four solutions have been prepared by adding the Pb^{2+} ions in the tap water and analyzed without any previous treatment. The obtained results are regrouped in Table 1. The recoveries founded are satisfactory and the relative standard deviation obtained after five measurements is of 3.32%. The percentage recovered obtained presented satisfactory values for the proposed electroanalytical methods [42] thus indicating the suitability of the proposed method for use in natural water samples. However, if the lead concentration is lower than $1.0 \times 10^{-8} \text{ mol L}^{-1}$, one must be aware that the recovery may be somewhat lower.

3.9. In domestic water

The same methodology has been applied with success in domestic water under the optimized conditions. Interference is possible because of the complexity of the matrix. Before use, the samples have been filtered through a membrane of $0.45 \mu\text{m}$ of diameter.

The comparison between the results obtained by the proposed methodology and the atomic adsorption spectroscopy reveals the capacity of HAp-CPE for the determination of these metals. The standard additions method has been used for the determination of lead in the domestic water samples. It should be mentioned at this point that the reason for using the standard addition technique is to compensate the matrix effect from domestic water samples that contain high concentrations of nitrate ions and other foreign ions as high as over thousand times of lead concentration. Hence, for the determination of lead in these samples by calibration method, the interferences of these ions impose errors on lead determination. Moreover, it is clear that there is not such difficulties in determining lead in tap water because of the simplicity of matrix in these samples. Four samples are prepared, $1 \times 10^{-8} \text{ mol L}^{-1}$ lead have been added in domestic water. Recovery experiments were also carried out in order to evaluate the interference of matrix effects of the domestic water samples on the detection of lead on HAp-CPE. Results obtained for R.S.D. and percentage recovery for the samples spiked with $1 \times 10^{-8} \text{ mol L}^{-1}$ lead were 4.10 and 96.5%, respectively. The results presented satisfactory values for the proposed electroanalytical methods indicating thus the suitability of the proposed method for use in domestic water samples. The presence of the

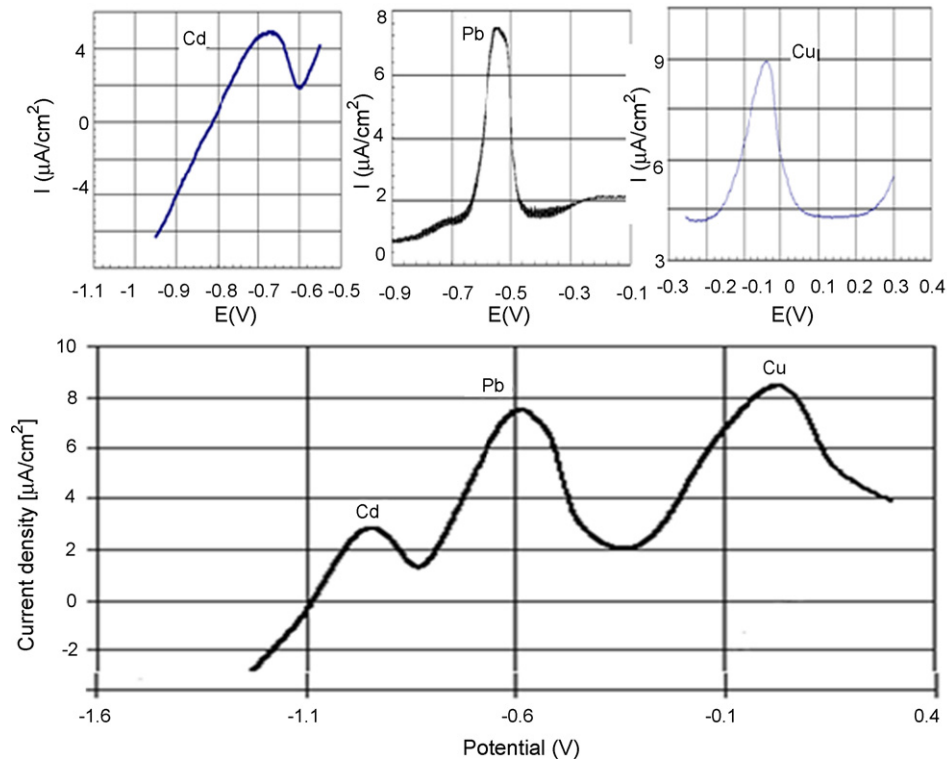


Fig. 9. Cyclic voltammograms of 1.2×10^{-7} mol L⁻¹ lead, cadmium and 1.6×10^{-7} mol L⁻¹ copper at 4% HAp-CPE, pH 7.0, 5 min of preconcentration time in 1.0 mol L⁻¹ HClO₄.

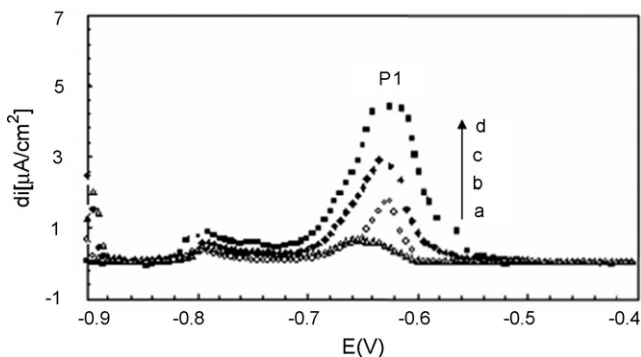


Fig. 10. Square-wave voltammograms in 1.0 mol L⁻¹ HClO₄ under the optimized conditions at HAp-CPE of lead(II): (a) 1.0×10^{-8} mol L⁻¹, (b) 2.0×10^{-8} mol L⁻¹, (c) 3.0×10^{-8} mol L⁻¹ and (d) 4.0×10^{-8} mol L⁻¹.

organic substances in the matrixes of the samples has a considerable effect on the response of lead at the electrode surfaces; it is due to the adsorption of such compounds on the apatite surfaces.

4. Conclusion

The determination of lead using a carbon-paste electrode modified with hydroxyapatite was improved when compared to unmodified CPE. The experimental conditions have been optimized and the response characteristics determined. The range for quantitative detection of lead was 2×10^{-9} mol L⁻¹ to 2.4×10^{-7} mol L⁻¹ with a preconcentration time of 7 min. These optimized characteristics will be the starting point for further investigations of the proposed sensor technique for lead detection in environment. Because of this, the electroanalytical methodology was applied in determining lead in spiked tap and domestic water, which witnessed different degrees of pollution.

The preconcentration of lead onto HAp-modified carbon-paste electrode is preceded by the substitution in the cationic site of apatite and the diffusion towards the interstitial liquid of the modified paste.

References

- [1] M.C. Neuman, A.W. Mcintosh (Eds.), *Metal Ecotoxicity, Concepts and Applications*, Lewis Publishers, Chelsea, MI, 1991.
- [2] J.O. Nriagu, J.M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, *Nature (London)* 333 (1998) 134.
- [3] K. Kalcher, J.M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, Sensors based on carbon paste in electrochemical analysis: a review with particular emphasis on the period 1990–1993, *Electroanalysis* 7 (1995) 5.
- [4] I. Švancara, K. Vytras, J. Barek, J. Zima, J. Barek, Carbon paste electrodes in modern electroanalysis, *Crit. Rev. Anal. Chem.* 31 (2001) 311.
- [5] R.O. Kadara, J.D. Newman, I.E. Tothill, Stripping chronopotentiometric detection of copper using screen-printed three-electrode system—application to acetic acid bioavailable fraction from soil samples, *Anal. Chim. Acta* 23 (2003) 95–104.
- [6] R. Kadara, I.E. Tothill, Resolving the copper interference effect on the stripping chronopotentiometric response of lead(II) obtained at bismuth film screen-printed electrode, *Talanta* 66 (2005) 1089–1093.
- [7] D. Demetriades, A. Economou, A. Voulgaropoulos, A study of pencil-lead bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry, *Anal. Chim. Acta* 519 (2004) 167–172.
- [8] L. Baldrianova, I. Svancara, M. Vlcek, A. Economou, S. Sotiropoulos, Effect of Bi(III) concentration on the stripping voltammetric response of in situ bismuth-coated carbon paste and gold electrodes, *Electrochim. Acta* 52 (2006) 481–490.
- [9] J. Wang, J.M. Lu, U.A. Kirgoz, S.B. Hocoar, B. Ogorevc, Insights into the anodic stripping voltammetric behavior of bismuth film electrodes, *Anal. Chim. Acta* 434 (2001) 29.
- [10] K. Vytras, I. Svancara, R. Metelka, A novelty in potentiometric stripping analysis: total replacement of mercury by bismuth, *Electroanalysis* 14 (2002) 1359–1364.
- [11] L. Baldrianova, I. Svancara, S. Sotiropoulos, Anodic stripping voltammetry at a new type of disposable bismuth-plated carbon paste mini-electrodes, *Anal. Chim. Acta* 599 (2007) 249–255.
- [12] M.A. Baldo, S. Daniele, Anodic stripping voltammetry at bismuth-coated and uncoated carbon microdisk electrodes, *Anal. Lett.* 37 (2004) 995.
- [13] C. Prior, C.E. Lenehan, G.S. Walker, Enhanced resolution of copper and bismuth by addition of gallium in anodic stripping voltammetry with the bismuth film electrode, *Electroanalysis* 18 (2006) 2486.
- [14] H. Zejli, K.R. Tamsamani, J.L. Hidalgo-Hidalgo de Cisneros, I. Naranjo Rodriguez, P. Sharrock, Electrochemical micro-extraction of lead(II) at a

- hydroxylapatite modified platinum electrode, *Electrochem. Commun.* 8 (2006) 1544–1548.
- [15] M.A. El Mhammedi, M. Bakasse, A. Chtaini, Square-wave voltammetric determination of paraquat at carbon paste electrode modified with hydroxyapatite, *Electroanalysis* 19 (16) (2007) 1727–1733.
- [16] M.A. El Mhammedi, A. Chtaini, A. El Bouadili, Comparative electrooxidation of formic acid and formaldehyde on Cu/Ca₁₀(PO₄)₆(OH)₂/Pd electrodes in acid medium, *ITE Lett. Batteries New Technol. Med.* 6 (1) (2005) B18–B21.
- [17] H.B. Lazrek, A. Rochdi, Y. Kabbaj, M. Taourirte, S. Sebti, Zinc chloride doped natural phosphate as 1-dipola cycloaddition catalyst, *Synth. Commun.* 29 (1999) 1057.
- [18] S.V. Prabhu, R.P. Baldwin, L. Kryger, Preconcentration and determination of lead(II) at crown ether and cryptand containing chemically modified electrodes, *Electroanalysis* 1 (1989) 13.
- [19] J. Wang, Z. Taha, N. Naser, Electroanalysis at modified carbon-paste electrodes containing natural ionic polysaccharides, *Talanta* 38 (1991) 81.
- [20] T. Molina-Holgado, J.M. Pinilla-Macias, L. Hernbdez-Hernbdez, Voltammetric determination of lead with a chemically modified carbon paste electrode with diphenylthiocarbazon, *Anal. Chim. Acta* 309 (1995) 117–122.
- [21] S.B. Hocevar, I. Svanera, K. Vytras, B. Ogorevc, Novel electrode for electrochemical stripping analysis based on carbon paste modified with bismuth powder, *Electrochim. Acta* 51 (2005) 706–710.
- [22] J.C. Elliott, *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*, vol. 18, Elsevier, Amsterdam, 1994, pp. 111–190.
- [23] D. McConnel, *Apatites, Applied Mineralogy*, vol. 5, Springer, New York, Vienna, 1963.
- [24] G. Wright, G. Montel, *C.R. Acad. Sci., Paris* 268C (1969) 2077–2080.
- [25] M.J. Kay, R.A. Young, A.S. Posner, Crystal structure of hydroxyapatite, *Nature* 204 (1964) 1050–1052.
- [26] J. Wang, B. Tian, Screen-printed stripping voltammetric/potentiometric electrodes for decentralized testing of trace lead, *Anal. Chem.* 64 (1992) 1706.
- [27] M.A. Baldo, S. Danele, G.A. Mazzocchin, A study on the suitability of carbon disk microelectrodes for trace analysis of lead and copper by ASV, *Electroanalysis* 10 (1998) 410.
- [28] K.Z. Brainina, I.V. Kubysheva, E.G. Miroshnikova, S.I. Parshakov, Y.G. Maksimov, A.E. Volkonsky, Small-size sensors for the in-field stripping voltammetric analysis of water, *Field Anal. Chem. Technol.* 5 (2001) 260.
- [29] D. Jagner, E. Sahlin, B. Axelsson, R. Ratana-Ophas, Rapid method for the determination of copper(II) and lead(II) in tap water using a portable potentiometric stripping analyser, *Anal. Chim. Acta* 278 (1993) 237.
- [30] M.A. El Mhammedi, M. Achak, M. Bakasse, A. Chtaini, Physico-chemical characterization of electrochemical deposit of Ca₁₀(PO₄)₆(OH)₂ on copper surfaces, *Appl. Surf. Sci.* 253 (2007) 5925–5930.
- [31] Hydroxyapatite [Ca₅(PO₄)₃(OH)] Joint Committee on Powder Diffraction Standards, Card No. 09-432.
- [32] J.C. Miller, J.N. Miller, Basic statistical methods for analytical chemistry. Part I. Statistics of repeated measurements, *Analyst* 113 (1988) 1351–1356.
- [33] M.F. Mousavi, A. Rahmani, S.M. Golabi, M. Shamsipur, H. Sharghi, Differential pulse anodic stripping voltammetric determination of lead(II) with a 1,4-bis(prop-2-enyloxy)-9,10 anthraquinone modified carbon paste electrode, *Talanta* 55 (2001) 305–312.
- [34] S. Laschi, I. Palchetti, M. Mascini, Gold-based screen-printed sensor for detection of trace lead, *Sens. Actuators B* 114 (2006) 460–465.
- [35] D. Purves, *Fundamental Aspects of Pollution Control and Environmental Science: Trace Elemental Contamination of the Environment*, vol. 7, Elsevier, New York, 1985.
- [36] B.O. Fowler, Infrared studies of apatites. I. Vibrational assignments for calcium, strontium, and barium hydroxyapatites utilizing isotopic substitution, *Inorg. Chem.* 13 (1) (1974) 194–207.
- [37] A. Bennouna, A. Khribech, J.P. Scharff, F. Chassagneux, B. Durand, O. Vittori, *Electrochim. Acta* 42 (17) (1997) 2659–2665.
- [38] R.C. Weast, M.J. Astle, *C.R.C. Handbook of Chemistry and Physics*, 63rd ed., 1982–1983, pp. B-111.
- [39] B. Sandrine, N. Angea, B.-A. Didier, C. Eric, S. Patrick, Removal of aqueous lead ions by hydroxyapatites: equilibria and kinetic processes, *J. Hazard. Mater.* A1 39 (2007) 443–446.
- [40] E. Mavropoulos, A.M. Rossi, A.M. Costa, C.A. Perez, J.C. Moreira, M. Saldanha, Studies on the mechanisms of lead immobilization by hydroxyapatite, *Environ. Sci. Technol.* 36 (2002) 1625–1629.
- [41] S. Bruckner, G. Lusvardi, L. Menabue, Effect of Cu²⁺ ion on the structural stability of synthetic hydroxyapatite, *J. Mater. Chem.* 3 (7) (1993) 715.
- [42] D. Dragoe, N. Spătaru, R. Kawasaki, A. Manivannan, T. Spătaru, D.A. Tryk, A. Fujishima, Detection of trace levels of Pb²⁺ in tap water at boron-doped diamond electrodes with anodic stripping voltammetry, *Electrochim. Acta* 51 (2006) 2437–2441.