



These methods, although highly sensitive, require relatively large volumes of sample for analysis, complicated operation, costly maintenance, expensive apparatus and low electrical power requirement [4].

Electrochemical methods are often used for environment monitoring including determination of pollutants including metal ions [5,6]. Lead as one part of heavy metals group pose a risk to human health and the environment due to its toxicity, because even exposure to low quantities can be life threatening [7,8]. Levels of lead are not stable in the environment and vary according to industrial production, urbanization, climate changes and many other factors [9]. The toxicity of lead in humans mainly arises from its mimicking action of occupying the calcium binding sites on numerous calcium-dependent proteins in cells resulting in the corresponding impairment of physiological functions [10,11].

Numerous analytical, bioanalytical, biochemical and biological instruments have been developed for determination of specific and/or group of compounds, species, cells even organisms, but most of them suffer from the impossibility to miniaturize these instruments in spite of the fact that they have many other advantages. Analysis in environment and biological monitoring brings one another requirement, and it is measuring of a large number of samples in short time. Due to the above-mentioned facts developing and suggesting of simple analytical instruments, methods and procedures with low detection limits and providing on-line and in situ monitoring of environment are needed [12].

Electrochemical methods are well known as very powerful techniques for determination of diverse range of metallic and biological targets in environmental, biological and industrial samples. Combining advantages of electrochemistry and fore-mentioned requirements led us to the suggestion of a new sensor array created with three-electrode system.

Modified electrodes are also attracting interest [12-14]. Recent works, reported in the literature, have shown several applications and electro analytical methodologies employing micro-electrodes as working electrodes [15-20].

Hydroxyapatite-modified platinum was recently used for the determination of lead with a detection limit of 5×10^{-7} mol.L⁻¹ [16], 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 analyses prior to voltammetric analysis gives rise to high selectivity and sensitivity. In the past, several kinds of modifiers carbon-paste electrodes have been used for lead determination [17-20].

In this work we prepared and characterized the lacunar-apatite 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^- [21-24].

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 lacunar-apatite $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5\text{OH}$ with molar ration $\text{Ca/P}=1.5$. Once lead comes in touch with the modified carbon paste, it is rapidly and strongly fixed to the lacunar-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 [25-28].

Experimental

All chemicals were of analytical grade and have been used as received without any further purification. All solutions were prepared in double distilled water. $\text{Pb}(\text{NO}_3)_2$ 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). The tricalcium phosphate apatite (TCP) with chemical formula: $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$ was prepared by reaction between calcium hydroxide ($\text{Ca}(\text{OH})_2$) and orthophosphoric acid (H_3PO_4) at room temperature and neutral pH. The preparation process was similar to our previous report [29].

Cyclic and square wave voltammetry were carried out with a Voltalab potentiostat (model PGSTAT 100, Ecochemie B.V., Utrecht, The Netherlands) driven by the general purpose of the electrochemical systems data processing software (voltalab master 4 software).

The electrochemical cell was configured to work with three electrodes by using TCP/CPE as the working electrode, platinum plate for counter and saturated calomel electrode (SCE) as reference electrodes. The whole cell modified carbon paste was subsequently packed firmly into the electrode cavity (0.1256 cm^2) and polished to a smooth shiny finish by gently rubbing over an ordinary weighing paper. Electrical contact was established with a bar of carbon. The resulting electrode is hereby denoted as TCP/CPE. The carbon paste electrode (CPE) alone was prepared in a similar way.

The initial procedure consisted in measuring the electrochemical response at the TCP/CPE electrode at a fixed concentration of lead $\text{Pb}(\text{NO}_3)_2$. The modified carbon paste electrode was immersed in a cell containing 20 ml of lead sample to get a chemical accumulation. Meanwhile, the solution was rotated at open circuit. After a desired preconcentration time, the electrode was removed from the preconcentration cell, rinsed with BDW and placed in the measurement cell containing the supporting electrolyte ($0.1 \text{ M Na}_2\text{SO}_4$). The solution was desecrated with nitrogen for 10 min.

The Lead $\text{Pb}(\text{NO}_3)_2$ supporting electrolyte was kept 20 s at open circuit before performing the voltammetric measurements. The square wave voltammetry was recorded in the range from -2.0 V to 2.0 V with a scan rate of 50 mV.s^{-1} , a step potential of 50 mV , the amplitude of 2 mV and 0.1 s duration. Optimum conditions were established by measuring the peak currents versus various investigated parameters such as preconcentration time, scan rate and concentration. All the experiments were performed at (25°C).

Results and Discussion

Surface chemical characterization

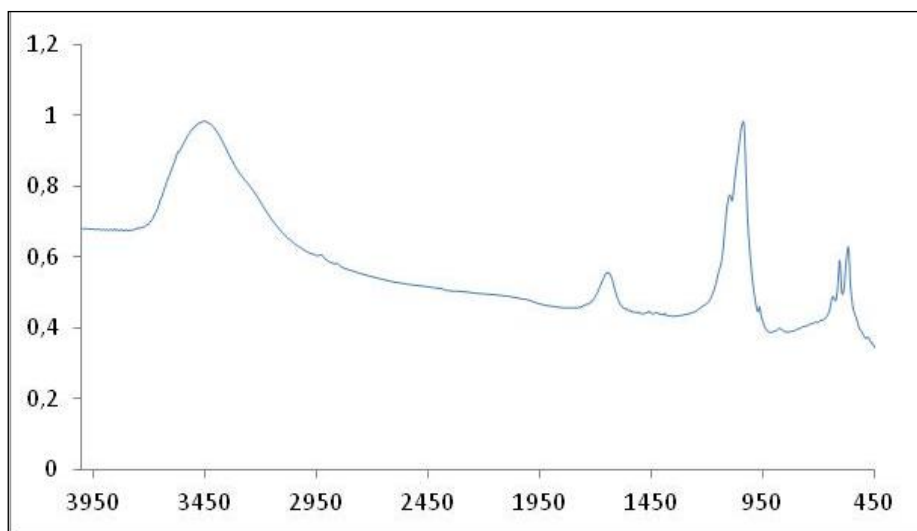


Figure 1: FTIR of powder dried at 105°C.

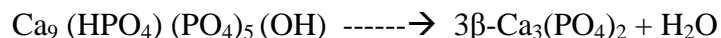
According to the infrared spectrum of the product dried at 105 °C (Fig.1), a characteristic band groupings HPO_4^{2-} is observed at 875 cm^{-1} which means the existence of the lacuna-apatite $[\text{Ca}_9 (\text{HPO}_4) (\text{PO}_4)_5 (\text{OH})]$. The TCP was identified by the bands of vibrations of groupings PO_4^{3-} which are: 474-571-962-1042 and 1087 cm^{-1} (Figure 1).

The elemental analysis of the tricalcium phosphate is shown in Table 1.

	Ca/P	%Ca	%P
TCP	1,499	34,174	17,616

Table 1: Chemical analysis of the tricalcium phosphate dried at 105°C.

The results of the elemental analysis show that the obtained product has a molar ratio of 1,499 which is very close to 1.5. This value characterizes the Beta-TCP material. To confirm this result, a XRD and FTIR spectrum analysis were performed. The XRD results (Figure 2), after the sintering process of the apatitic TCP at 900°C, show the presence of the Beta-TCP (fichier PDF N° 009-0169). A disappearance of the anion HPO_4^{2-} , was observed in this calcination which can be explained by the transformation of the lacunar-apatitic phosphate to β -TCP thermal phase. The reaction of this transformation is as follows:



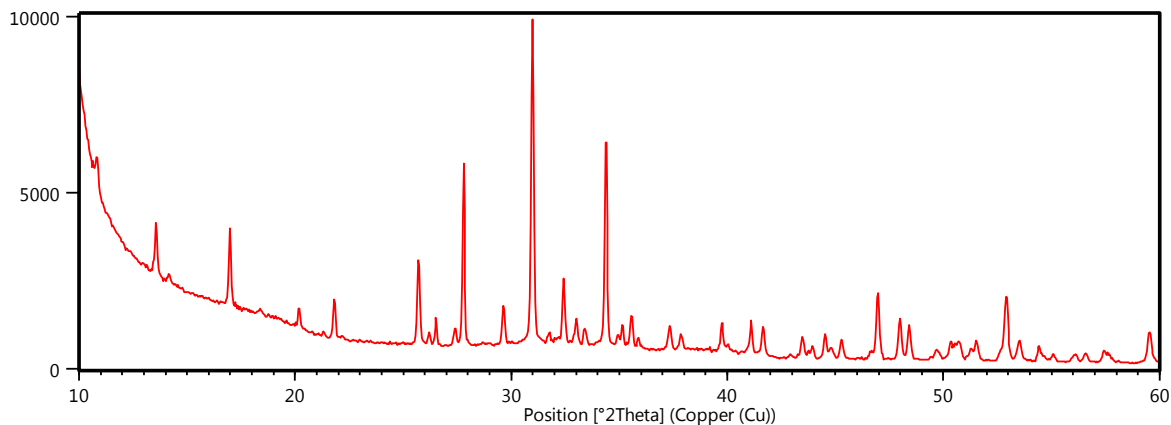


Figure 2: X-ray diffraction of beta-TCP calcined at 900°C.

Surface Electrochemical Characterization

The cyclic voltammograms of both unmodified carbon paste electrode (CPE) and TCP/CPE are shown in Figure 1 (inset graph). The TCP/CPE voltammogram showed that the modified electrode is electro inactive at a reasonable broad potential range of approximately -2000 mV to 2000 mV. In the preconcentration step, the accumulated Pb^{2+} was found to be reduced at 0.1 V at which the lead ion is electrochemically deposited at the electrode surface. The deposited lead is oxidized at -0.3 V (Figure 3).

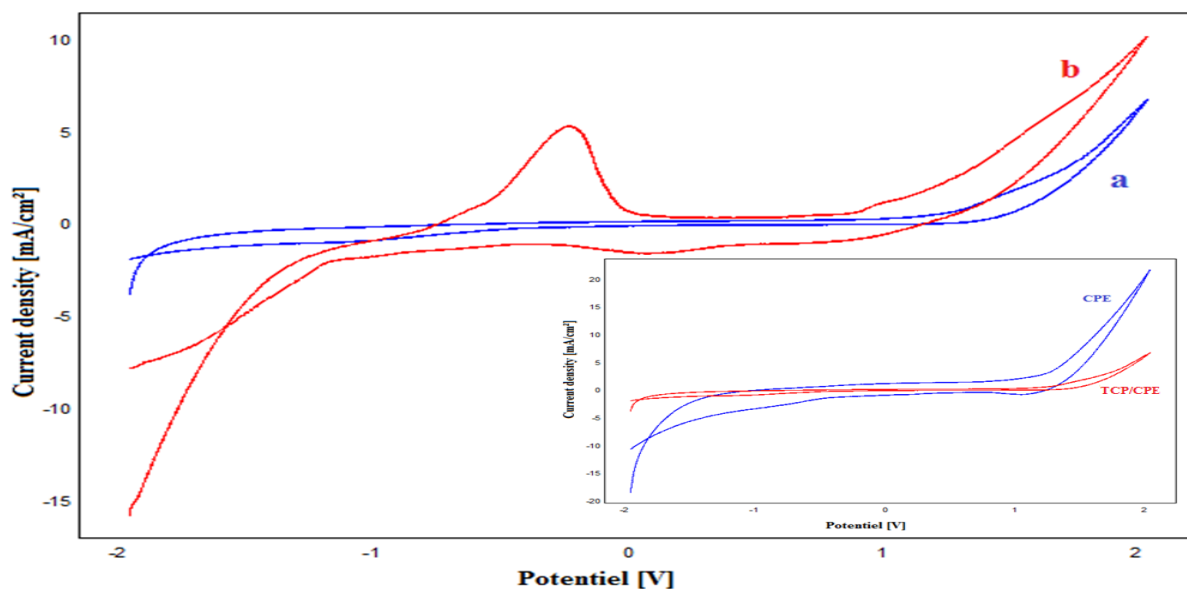


Figure 3: Cyclic voltammograms recorded on the TCP/CPE containing 0.1 M Na_2SO_4 at a scan rate of 100 mV/s: (a) In absence and (b) after accumulation of Pb^{2+} . (Inset): Voltammograms of CPE and TCP/CPE in 0.1 M Na_2SO_4

Effect of Scan Rate

In Figure 4, it is noticed that the Pb^{2+} is oxidation peak increases with the potential scan rates. A linear dependency of the anodic current peak on the scan rate was observed from the plot of i_{pa} versus the potential scan rates over the range of 10 to 150 $mV.s^{-1}$.

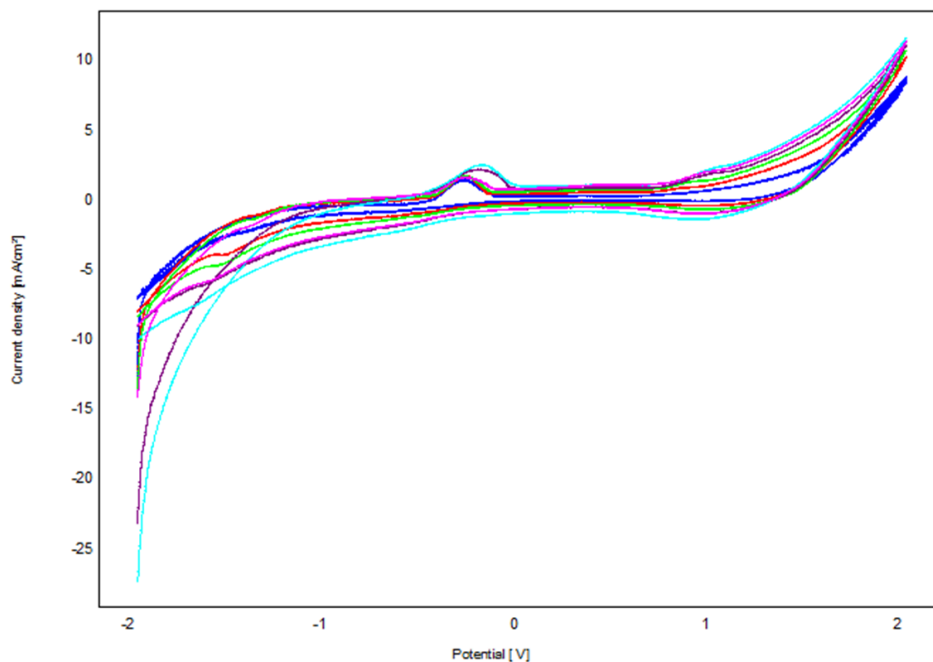


Figure 4: Cyclic voltammograms acquired on TCP/CPE with $6 \times 10^{-3} \text{ mol.L}^{-1}$ of Lead (pH=7.0) in 0.1 M Na_2SO_4 supporting electrolyte at different scan rates from 10 to 150 mV/s.

In Figure 5, the correlation coefficient of the obtained straight line is about 0.96. Hence it can be deduced from the obtained result that a surface process involving adsorption of Pb^{2+} occurs prior to its oxidation.

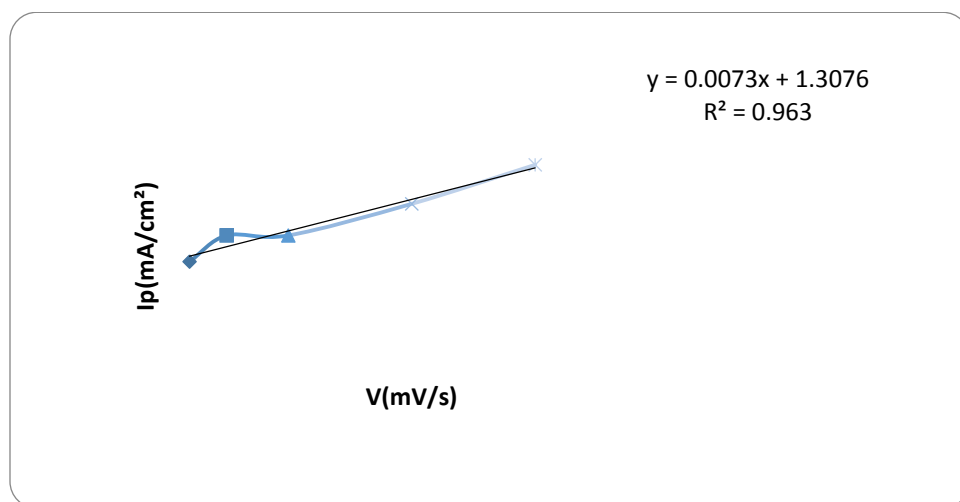


Figure 5: Plot of peaks area versus scan rate

Surface chemical characterization of the microelectrode before and after addition of Pb:

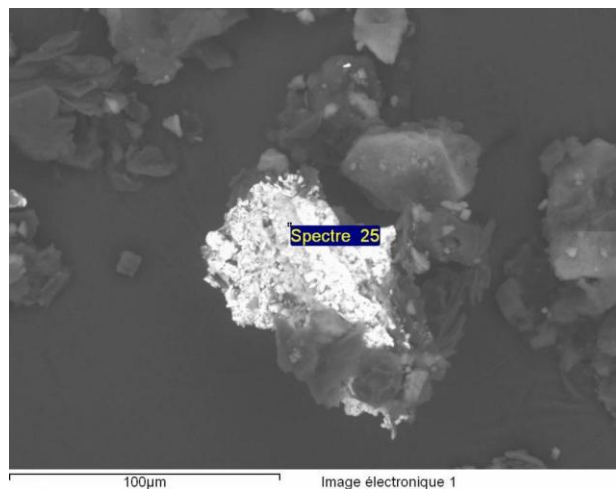
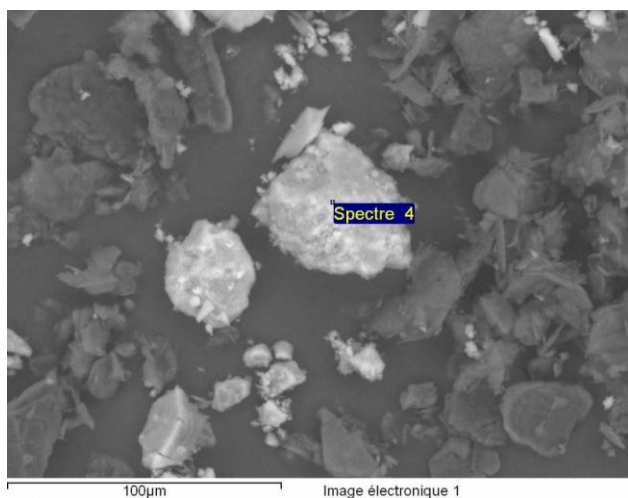


Figure 6(a): SEM image of the TCP/CPE before addition

Figure 6(b): SEM image of the TCP/CPE after addition

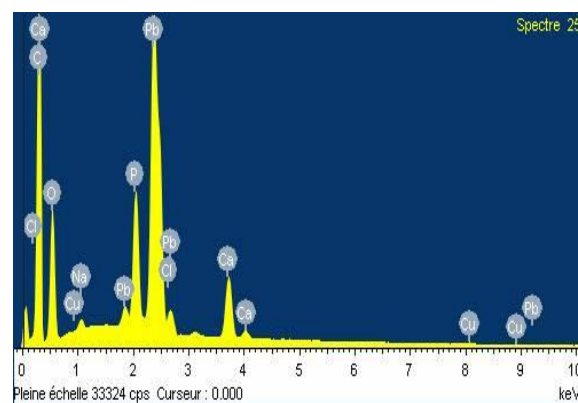
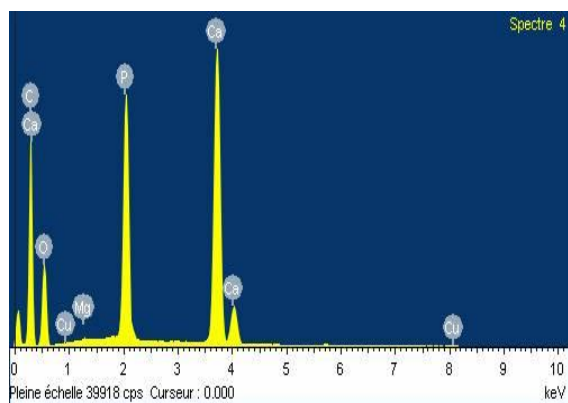


Figure 7(a): EDAX spectrum of the TCP/CPE before addition

Figure 7(b): EDAX spectrum of the TCP/CPE after addition of Pb.

The analysis resultants of SEM/EDAX show the morphology and composition of the microelectrode before and after addition of Pb^{2+} . This phenomenon causes the decrease of calcium's peak, while the peak of Pb has appeared. This result is confirmed by the surface morphology of the TCP/CPE microelectrode was carried out by SEM. In Figures 6 and 7 we observed a clear layer corresponds to the deposit of the Pb on the microelectrode.

Optimization of Experimental Conditions

Optimum conditions for the electrochemical response were established by measuring the peak current in dependence on all parameters.

Influence of Accumulation Time

The effect of pre-concentration time on the voltammetric response for 6×10^{-3} M of Pb^{2+} using TCP/CPE electrode, is shown in Figure 8, The response current increased as deposition time increased from 0 to 15 min. After this period, the peak current did not change significantly with time. Besides, these results indicate that the sorption process can be considered very fast within the first 15 min of adsorption. This phenomenon can be attributed to the saturation of Pb^{2+} at the prepared electrode surface. Taking into account the sensitivity and the efficiency, accumulation time was 15 min in the following experiments.

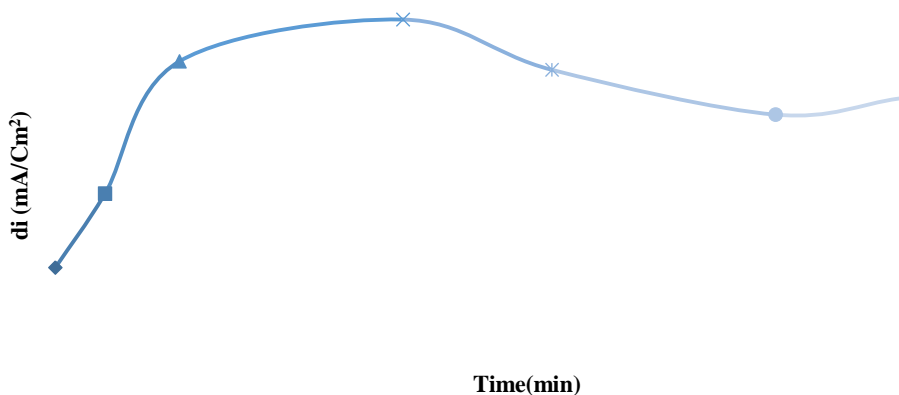


Figure 8: Influence of preconcentration time on the peak intensity of 6×10^{-3} mol. L^{-1} Lead (pH=7.0) on SWV at TCP/CPE in 0.1 M Na_2SO_4 with 50% of TCP/CPE ratio.

Calibration Plots

The determination of Pb^{2+} at the TCP/CPE was performed by using cyclic (CV) and square wave voltammetry (SQW). The SQW obtained for different concentrations of lead present two peaks at, successively, at -0.8 V and -0.5 V (Figure 9) the first one was associated to the oxidation of deposited Pb, the second one to the reduction of accumulated Pb^{2+} .

In its inset, a linear evolution of the peak current density toward the Pb^{2+} concentration was reached. As it is obtained, the oxidation peak current (I_p) is proportional to Pb^{2+} concentration in the range of 3×10^{-3} M to 21.13×10^{-3} M with a detection limit (DL, 3 SD) of 4.3×10^{-6} M and a quantification limit (QL, 10 SD) of 1.43×10^{-5} M. Under the optimized conditions, the relationship between the peak current density of Pb^{2+} and its concentration is linear with a regression equation of $I(mA) = 0.005 [Pb^{2+}] + 0.365$ ($R^2 = 0.906$).

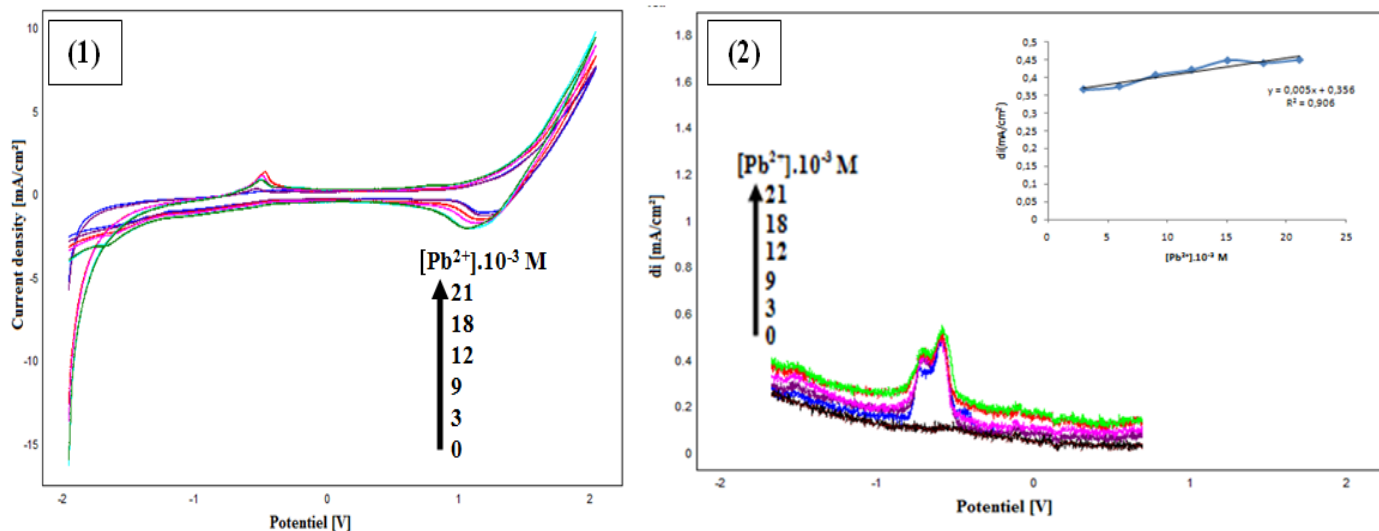


Figure 9: Cyclic (1) and (2) Square wave voltammograms at TCP/CPE in 0, 1 M Na_2SO_4 for different concentrations of Pb^{2+} . Scan rate 100 mV/s.

Influences of pH

The influence of pH on the determination of lead was also investigated Figure 10 as the pH increased from pH 2.0 to 7.0, the peak current increased at first because TCP is probably 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 7.0. After this period, as can be seen, the peak current gradually reduces with the increase of pH.

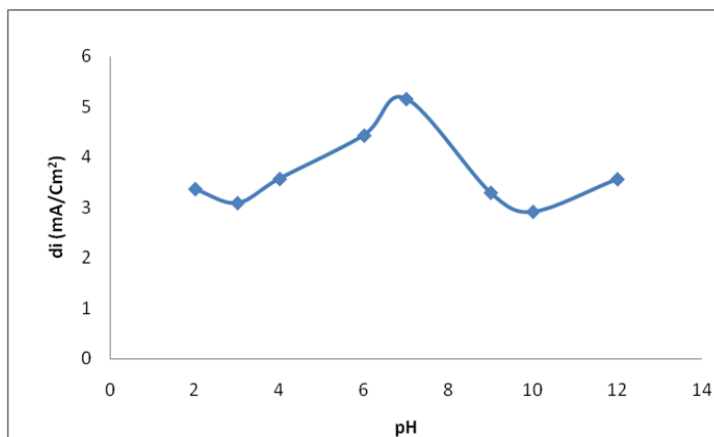


Figure 10: Effect of the pH on SWV peak height of $6 \times 10^{-3} \text{ mol L}^{-1}$ lead in 1.0 mol L^{-1} Lead (pH=7.0) on SWV at TCP/CPE in $0.1 \text{ M Na}_2\text{SO}_4$ with 50% of TCP/CPE ratio.

Influence of the Content of TCP in Carbon-paste Mixture % (w/w)

The effect of the carbon paste composition in the voltammetric response of the microelectrode modified with TCP was evaluated by square-wave voltammetry of $6 \times 10^{-3} \text{ mol L}^{-1}$ Pd (II) in $0.1 \text{ M Na}_2\text{SO}_4$ (Figure 11). The anodic peak current increased with the amount of apatite in the paste up to 5% (w/w). Beyond the anodic peak current decreased significantly, this probably occurs due to a decrease in the conductive area at the electrode surface.

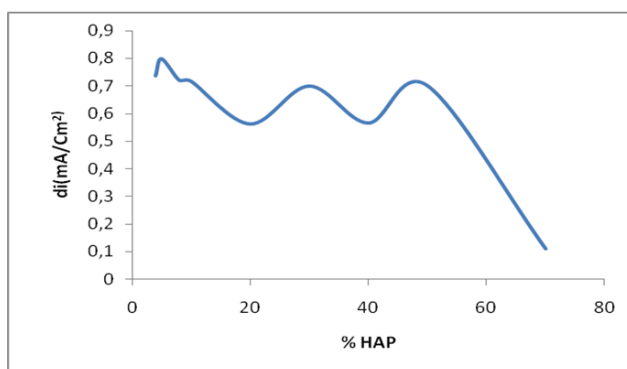


Figure 11: Influence of the content of TCP in carbon-paste mixture % (w/w) on SWV peak currents of $6 \times 10^{-3} \text{ mol L}^{-1}$ lead in $0.1 \text{ M Na}_2\text{SO}_4$, $t_p = 15 \text{ min}$, $\text{pH } 7.0$.

Interference Studies

We tested the elements that can present a certain competition to the level of the sites on TCP/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 TCP/CPE in aqueous solutions of the nitrate of lead, cadmium and zinc (Figure12). The anodic oxidization of the cadmium occurs to the potential of -0.8 V/SCE , lower to the potential oxidation of lead -0.5 V/SCE . The oxidization peak of zinc appears at a potential -1.2 V/SCE . The clean separation of the three potential peaks offers us the possibility of the simultaneous determination of lead, cadmium and zinc.

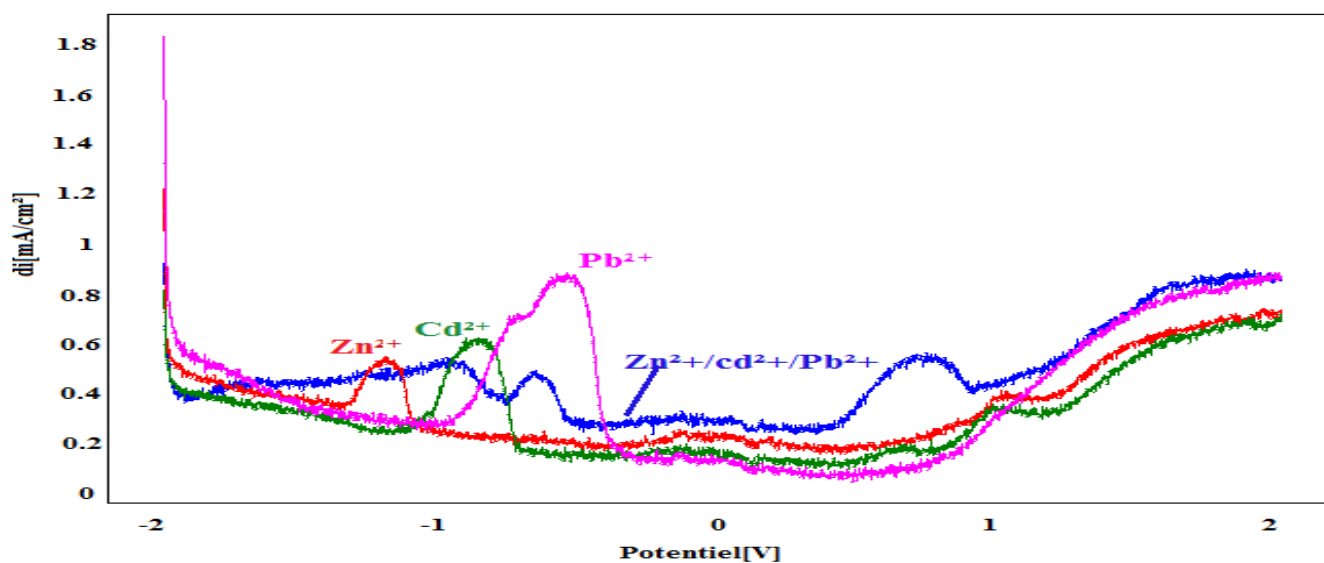
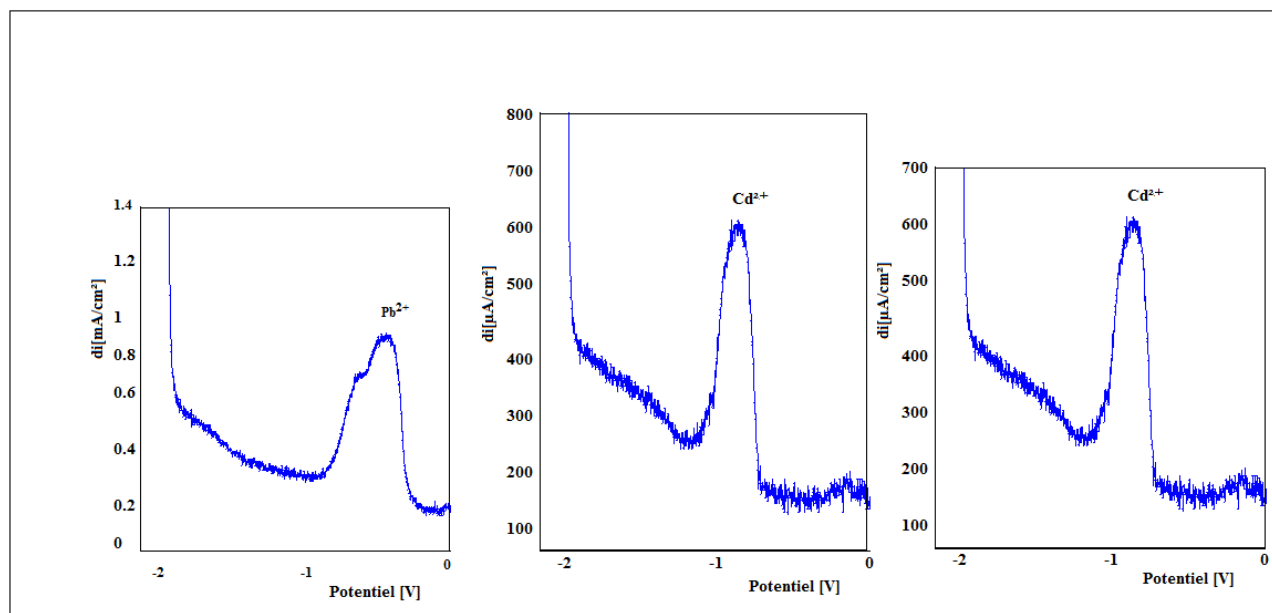


Figure 12: Cyclic voltammograms of 10 mg/L lead, 10 mg/L cadmium and 10 mg/L zinc at TCP/microelectrode, pH 7.0, 15 min of preconcentration time in 0.1 M Na₂SO₄.

Conclusion

This work has determined the optimum operating conditions by a simple and fast electrochemical process to find the concentration of the aqueous medium in the Lead thanks to a Carbon paste microelectrode modified by apatitic tricalcium phosphate (TCP). The electrochemical results described above show the electrochemical adsorption's response of the Pb²⁺ on the microelectrode of TCP/CPE. These modified microelectrodes can be used as sensors for the detection of traces of heavy metals such as cadmium, lead and zinc in different solutions.

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