Original Article

Electrochemical determination of iron(II) at a Nafion-1,10-phenanthroline-modified carbon paste electrode: Assessing the correlation between preconcentration potential, surface morphology and impedance measurements

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Abstract : The electrochemical behavior of a Nafion-1,10-phenanthroline-modified carbon paste electrode (CMCPE: Chemically Modified Carbon Paste Electrode) immersed in a supporting electrolyte 0.1 mol.L^{-1} acetate buffer solution (pH 4.5) containing iron(II) metal ion has been studied, using cyclic voltammetry, differential-pulse voltammetry and impedance spectroscopy. Optimal analytical parameters (preconcentration potential and time, pH, electrode rotation) for iron(II) metal ion determination have been established and correlated with the surface morphology of the CMCPE surface, the chemical composition analysis of the surface and the impedance measurements of the CMCPE immersed in the supporting electrolyte. Assuming a simple approach based on a redox polymer-modified electrode, the experimental impedance values were fitted to an equivalent circuit model. It was shown that among various potentials used for iron(II) accumulation in the Nafion-film, the potential of +1.3 V vs. Ag/AgCl/3 mol. L^{-1} KCl allowed a better differential-pulse determination of the examined iron(II) metal ion in the supporting electrolyte. The work was expanded to real applications with the determination of iron(II) metal ion in groundwater samples collected in a village located at the outskirts of Ouagadougou, the Capital of Burkina Faso.   **© Global Scientific Inc.**

Keywords : Iron(II) metal ion; Nafion-1,10-phenanthroline-modified carbon paste electrode; Differential-pulse voltammetry; Impedance measurements.

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INTRODUCTION

Stripping Voltammetric methods have been applied to the determination of many elements such as metal ions because of their low cost, easy operation, good sensitivity, high selectivity and very low limits of detection[1]. Numerous advantages that have been reached in such measurements include the following: needless of preliminary separations, low level of contamination, and possibility of distinction between different redox and or binding states[1-7]. Different techniques of stripping voltammetry consist in a preconcentration step onto the electrode and a further voltammetric measurement. As a consequence, voltammetric determinations can be greatly improved with respect to sensitivity and selectivity[2].

The most current approaches based on stripping procedures include anodic or cathodic stripping voltammetry (ASV or CSV) at both a hanging mercury drop electrode (HMDE) and a thin mercury film electrode (MFE)[8-12]. However, due to the toxicity of mercury and difficulties related to the determination of metal ions that do not form amalgam with mercury, techniques using mercury free-electrode have been developed. These techniques included not only ordinary solid electrodes such as glassy carbon, carbon paste, gold, bismuth film, carbon film but also chemically modified electrodes[13-30]. Chemically modified electrodes (CME) generated a great interest since the mid-1970s[31,32], and have been employed by several groups to enhance sensitivity and selectivity of voltammetric measurements for the determination of metal ions, organic and bio-organic species. Among these, chemically modified carbon paste electrodes (CMCPEs) have shown well-recognized advantages because they are very easy to make and can be prepared with a variety of modifier loading levels, and they show a low background current[2,3,33-35]. Moreover, fresh modified-electrode surface can be generated rapidly and reproducibly[2,3]. Many groups have reported the use of CMCPEs in the field of electroanalysis.

Baldwin and co-workers used carbon paste electrode modified by 2,9-dimethyl-1,10-phenanthroline for the detection of copper and nickel[23,24]. The 2-methyl-8-hydroxyquinone has been used as a modifier agent for the detection of copper[36]. Incorporation of poly (1,8-diaminonaphtalene) in carbon paste electrode leading to a conducting polymer has been demonstrated and used for the determination of lead[37]. Silver[38,39] and gold[40,41] have been determined using ion-exchanger-and chelating resin-modified carbon paste electrodes. Determination of metal ions by ion-exchange using typical resins in carbon paste has been reported[42,43]. Lead (II) and Cadmium (II) have been determined at a diaceyldioxime modified carbon paste electrode by differential pulse stripping voltammetry[44]. Monomeric and polymeric cyclodextrins modified carbon paste electrodes have been investigated for the determination of carcinogenic polycyclic aromatic amines[45]. Electrochemical determination of iron metal ions has been the subject of several studies[2,3,9,10,29,30]. Zhao and co-workers described a new concept for the differential pulse voltammetric determination of iron(II), based on complexation of the metal ion by a modifier reagent, 1,10-phenanthroline, and then accumulation in an ion-exchanger (Nafion) incorporated in the carbon paste electrode[2]. They also reported the differential pulse voltammetric determination of iron(II) at a Nafion-film-coated carbon paste electrode, based on the formation of the 2,2'-bipyridyl complex of the metal ion and its accumulation in the Nafion film at the electrode[3]. However, all the previous studies didn't report the use of impedance techniques for the characterization of the as-prepared electrochemical sensor implemented for trace iron determination. As electrochemical impedance techniques have become an important tool when investigating the electrochemical properties of modified electrodes[46-51], the present work also included this study in the case of iron incorporated in a Nafion-1,10-phenanthroline-modified carbon paste electrode. To the best of our knowledge, impedance techniques have not been used to characterize trace iron incorporated in the Nafion-1,10-phenanthroline-modified carbon paste. Moreover, any correlations have not yet been established between the preconcentration potential used for the metal ion incorporation into the Nafion-1,10-phenanthroline-modified carbon paste electrode, the surface morphology and the impedance measurements. It is clear that such correlations may appear important, both from a fundamental and applied standpoint, when investigating complexation and adsorption processes on electrode surfaces, electron transfer and reaction

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mechanism, kinetics of electron transfer processes. Since the performance of the electrochemical sensor depends greatly on the parameters of these surface processes, one must be careful to understand fully their role in the whole process before using the sensor for analytical determination in different environmental matrices. Although the Nafion-1,10-phenanthroline-modified carbon paste electrode has already been used for iron(II) determination at the laboratory scale, we think that more data are needed in developing country to assess their analytical utility by application to real-life groundwater samples in rural environment where concentrations of iron(II) metal ions, which are higher than the guideline values in drinking water given by the World Health Organization (WHO), are detected.

The present work was prompted by a desire to revisit the field of Nafion-film-coated carbon paste electrode in voltammetric determination of iron(II) with two objectives. The first one was to characterize the sensor by electrochemical impedance spectroscopy as well as by cyclic voltammetry and differential-pulse voltammetry in order to obtain mechanistic information related to the oxidation and reduction of ferroïn ($Fe(phen)_3^{3+}$/$Fe(phen)_3^{2+}$) system into the modified carbon paste electrode. The sensor is prepared by using the complexation of iron(II) with a reagent modifier, 1,10-phenanthroline, and then accumulation by an ion-exchanger (Nafion) incorporated in the carbon paste electrode. However, in our context the previous procedure described by Zhao and co-workers[2] was combined with the spin-coating technique[52,53]. We expected that better and enhanced peak currents could also be achieved with these two combined procedures. Great efforts were made to understand impedance measurements at the interface, and to correlate them with the preconcentration potential applied for iron incorporation into the Nafion -1,10-phenanthroline-modified carbon paste electrode. Data obtained from impedance analysis allowed the proposal of a scheme describing charge transfers at the Nafion-1,10-phenanthroline-modified electrode. The surface morphology of the chemically modified carbon paste electrode was also investigated and linked to the optimal analytical conditions for iron(II) determination. The second objective of this work was to demonstrate the performance of the sensor by application to the determination of iron(II)

contents in various real groundwater samples collected in a village located at the outskirts of Ouagadougou, the Capital of Burkina Faso. The results obtained constitute the first study of iron(II) determination at groundwater sites in Burkina Faso and will provide a baseline of spatial and temporal changes of iron(II) pollution in the country.

EXPERIMENTAL

Reagents and solutions

All chemicals were of analytical grade. An iron(II) stock solution was prepared by dissolving the required amount of ammonium iron(II) sulphate (99.999 %, Sigma Aldrich) in 0.01 mol.L^{-1} sulphuric acid (96.3 % VWR). Diluted working solutions for optimization studies were prepared by diluting the stock solution with Millipore water.

1,10-phenanthroline (99 %), paraffin oil and Nafion solution 5 wt % (d = 0.924) were purchased from Sigma Aldrich. Graphite powder (99.9995%) was purchased from Alfa Aesar.

Apparatus, cell and electrodes

The electrochemical experiments (cyclic and voltammetric measurements) were carried out using a Voltalab 50 PGstat potentiostat (Radiometer, Copenhague) running with the VoltaMaster software (version 4.0). The voltammetric cell (25 mL) consisted in a MDE 150 stand (Radiometer Model) with an EDI 101 rotating disk modified carbon paste electrode, an Ag/AgCl, 3 mol.L^{-1} KCl reference electrode (Eref = 0.205 V / NHE; Radiometer model TR020) and a platinum wire as the counter electrode (radiometer model TM020).

Impedance measurements were obtained with a μAUTOLABIII/FRA (Eco Chemie, Netherlands) driven by the FRA software. All experiments were carried out at room temperature (25°C). Measurements have been carried out at the free potential of the interface, in a frequency range between 50 mHz and 50 kHz and with the perturbation amplitude of 10 mV.

The chemically modified carbon paste electrode (CMCPE) was made by thoroughly mixing appropriated amounts of 1,10-phenanthroline 10 wt % (Sigma Aldrich) and Nafion solution 5 wt % (d = 0.924, Sigma

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Aldrich) with 1 g of graphite powder (99.9995 %, Alfa Aesar) in a first step, and then mixing with 0.360 mL of paraffin oil in a second step using a mortar and pestle until a uniformly wetted paste was obtained. The paste was inserted into the cavity of the electrode (EDI Tip). The chemically modified carbon paste surface was smoothed on a transparent paper until the surface took a shiny appearance. Then the electrode surface was coated with the Nafion by a spin-coating technique using a methanolic solution of Nafion (400 µL of Nafion in 300 µL of pure methanol). Using a micro syringe, about 4 µL of the methanolic was placed on the electrode surface. The electrode was spun at a rotation of 1000 rpm after deposition of the Nafion coating solution, maintaining the EDI disc in an upward position. The surface was then kept ten minutes at room temperature to let the solvent evaporate. This spin-coating procedure allows a better surface preparation[52,53]. The electrode surface could be renewed by simply extruding a small amount from the tip of the electrode.

Surface morphology analysis of the electrodes (bare carbon paste electrode, modified carbon paste electrode and iron(II)-modified carbon paste electrode) was carried out using a scanning electron microscopy (SEM HITACHI computer-controlled with the software TM-100) coupled with an EDX (software SwiftED-TM) for chemical analysis of electrode surfaces.

Recommended analytical method

The supporting electrolyte solution (20 mL), containing the acetate buffer (pH 4.5) and the examined iron(II) ion at a given concentration, was pipetted into the micro-voltammetric cell. A fresh electrode surface was immersed in the supporting electrolyte solution and a defined preconcentration (accumulation) potential was applied to the CMCPE for a selected time period, while the rotating disk electrode (RDE) was under rotation at 1000 rpm. At the end of the preconcentration time, the rotation of the electrode was stopped and the solution was left to equilibrate for 30 s. The voltammogram was then recorded by scanning the potential in the cathodic direction using cyclic and differential pulse voltammetry. The parameters used for the differential voltammetry were a potential step height of 1 mV, pulse amplitude of 60 mV and duration of 20 ms. Recovery of Fe(II) in the analyzed samples was estimated using the standard

addition methods by introducing aliquots of iron standard solution and recording the corresponding differential-pulse voltammograms. After each electrochemical determination, the cleaning procedure of the electrode surface was the following: transferring of the electrode in 1.0 mol.L^{-1} sodium hydroxide solution under stirring for several minutes and then rinsing thoroughly with water and immersing in a stirred blank acetate buffer solution of pH 4.5 (NaOAc/AcOH)[2].

All the measurements were carried out at room temperature (25°C) and without solution deoxygenating. Measurements were automated and controlled through the software parameters. In this work, the anodic contribution of current is taken as positive and the cathodic one as negative.

RESULTS AND DISCUSSION

Electrochemical behavior of iron(II) on the chemically modified carbon paste electrode

The first step of our investigations was to assess whether the spin-coating procedure[52,53] combined with the one described in the literature[2] could lead to significant results in differential-pulse peak current measurements of trace iron(II) in a sample solution. We first set the experimental conditions as previously described: 1 g of graphite powder was mixed with the desired weights of 1,10-phenanthroline and Nafion solution, and then mixing with paraffin oil[2]. By varying the amount of reagents in the carbon paste, we found that the optimum conditions were the following: 1,10-phenanthroline 10 wt % and Nafion solution 5 wt %. The as-prepared Nafion-1,10-phenanthroline-modified carbon paste electrode was cleaned and the differential-pulse voltammogram was recorded between 1.3 V and 0.5 V (Figure 1a), after immersing the electrode in a solution containing the acetate buffer (pH 4.5) and the examined $10^{-5} \text{ mol.L}^{-1}$ iron(II) ion and following a pretreatment of the electrode at a potential of 1.3 V applied for 4 minutes. The differential-pulse voltammogram in Figure 1b was recorded in the same conditions as in Figure 1a, except that in this case the surface of the Nafion-1,10-phenanthroline-modified carbon paste electrode was coated with the Nafion by a spin-coating technique using a methanolic solution of Nafion (400 µL of Nafion in 300 µL of pure methanol). The spin-coating

rotation was fixed at 1000 rpm. As can be seen in Figure 1, a better and enhanced peak current (Figure 1b) is obtained when the Nafion coating solution was spin-coated on the initial Nafion-1,10-phenanthroline-modified modified carbon paste electrode surface. This procedure allowed a better surface preparation. As a consequence, electrodes (CMCPE) prepared with this method were used in all subsequent work.

In a second step, the voltammogram of the Nafion-1,10-phenanthroline-modified carbon paste electrode (CMCPE) immersed in 0.1 mol.L^{-1} acetate buffer (pH 4.5) was recorded. The electrode potential was scanned between 1.3 V and 0.5 V (Figure 2a, b, c and d). The voltammograms obtained without pre-electrolysis at 1.3 V (Figure 2a) or following a pretreatment at a potential of 1.3 V applied for 4 minutes (Figure 2b) exhibit no voltammetric peaks. The same previous experiences were repeated for a solution containing the acetate buffer (pH 4.5) and the examined 10^{-5} mol.L^{-1} iron(II) ion. While the voltammogram in Figure 2c, recorded without a preconcentration potential, shows no well defined

voltammetric signals, the one in Figure 2d, recorded following a preconcentration potential, displays the classic curve of an electrochemical system. Figure 2e displays the voltammogram in the same conditions as in Figure 2d, except that after the preconcentration potential of 1.3 V applied at the CMCPE, the electrode potential was scanned between 0.5 V and 1.3 V. As can be seen the same electrochemical system of Figure 2d is detected in Figure 2e. These preliminary results suggest that an applied preconcentration potential is necessary for incorporation of the iron ion into the Nafion-coated carbon paste electrode. This is supported by the fact that a voltammogram (not shown), recorded following a preconcentration at open circuit potential in the acetate buffer (pH 4.5) containing the examined 10^{-5} mol.L^{-1} iron (II) ion, exhibits no redox waves, neither in the cathodic direction (1.3 V to 0.5 V) nor in the anodic one (0.5 V to 1.3 V). Taking into account the potentials of the cathodic and anodic peaks, the redox potential is evaluated $E° = (Ep_{cathodic} + Ep_{anodic})/2 = 0.85$ V. In agreement with the literature[2]
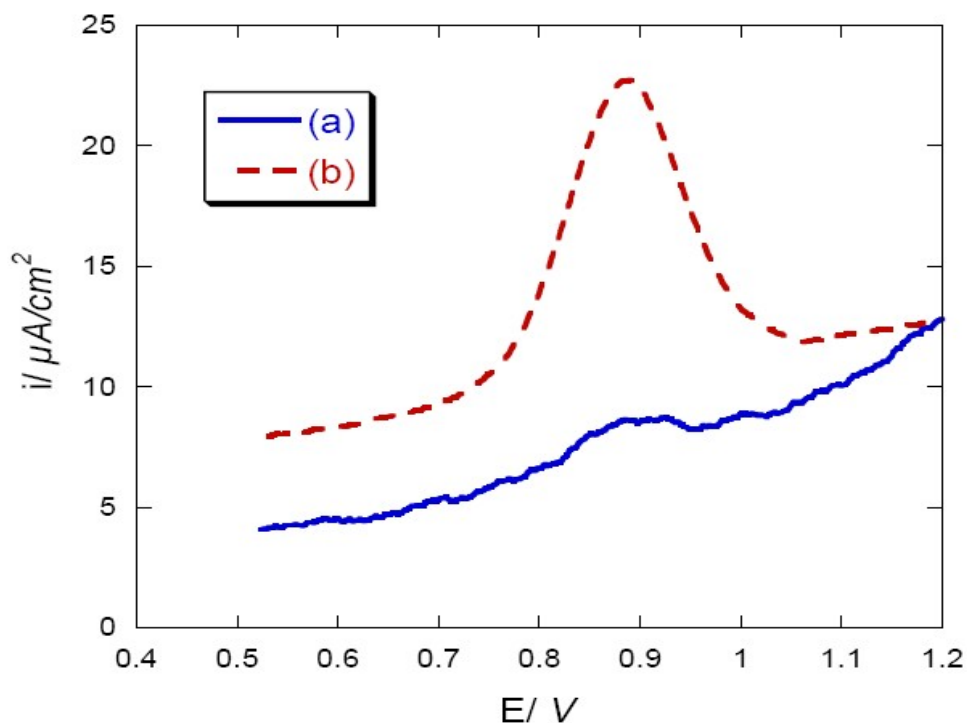

Figure 1 : Differential-pulse voltammetry in 0.1 mol.L^{-1} acetate buffer (pH 4.5) containing 10^{-5} mol.L^{-1} iron(II) of Nafion-1,10-phenanthroline-modified carbon paste electrode: a) the modified carbon paste electrode was prepared by mixing 1 g of graphite powder with 1,10-phenanthroline 10 wt % and Nafion solution 5 wt %, and then mixing the powder with paraffin oil; b) same preparation as in a) and a Nafion coating solution was spin-coated on the electrode surface (spin-coating rotation of 1000 rpm). In both cases the voltammograms were recorded following a pretreatment of the electrode at a potential of 1.3 V applied for 4 minutes, the electrode being under rotation at 1000 rpm.

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and the redox potential of ferroïn (Fe(phen)$_3^{3+}$/Fe(phen)$_3^{2+}$), $E° = 1.06$ V / NHE $= 0.86$ V / Eref), the electrochemical system observed in Figures 2d and 2e is assigned to the tris(phen)iron couple (ferroïn couple). Using a simple model of a redox polymer-modified electrode[52], one may suggest that during preconcentration, Fe^{2+} diffuses through the Nafion polymer and is oxidized into Fe(phen)$_3^{3+}$ in the carbon paste electrode. The potential scan gives the evidence of the reversible electron transfer:

$$Fe(phen)_3^{3+} + e_{electrode}^- \underset{\leftarrow}{\overset{\rightarrow}{\rightleftharpoons}} Fe(phen)_3^{2+}$$

Nafion is a perfluorosulphonate cation-exchange resin with RSO$_3^-$ sites. The iron Fe^{2+} can be exchanged and accumulated by Nafion by forming complexes with RSO$_3^-$ sites in the Nafion-modified electrode film[2]. Through the Nafion-film, the iron Fe^{2+} can diffuse[52] and be complexed by phenanthroline in the carbon paste electrode. That is why in Figure 2c, the ferroïn system can be guessed in the residual current. Furthermore, by applying an anodic preconcentration potential of 1.3 V at the CMCPE, the iron Fe^{2+} which is complexed into Fe(phen)$_3^{2+}$ is oxidized into Fe(phen)$_3^{3+}$ in the carbon paste electrode. This process induces the accumulation of Fe(phen)$_3^{3+}$ and an iron Fe^{2+} flow through the Nafion film. Then scanning the electrode potential in the (1.3 V to 0.5 V) domain shows the reduction of the accumulated Fe(phen)$_3^{3+}$ and its reoxidation.
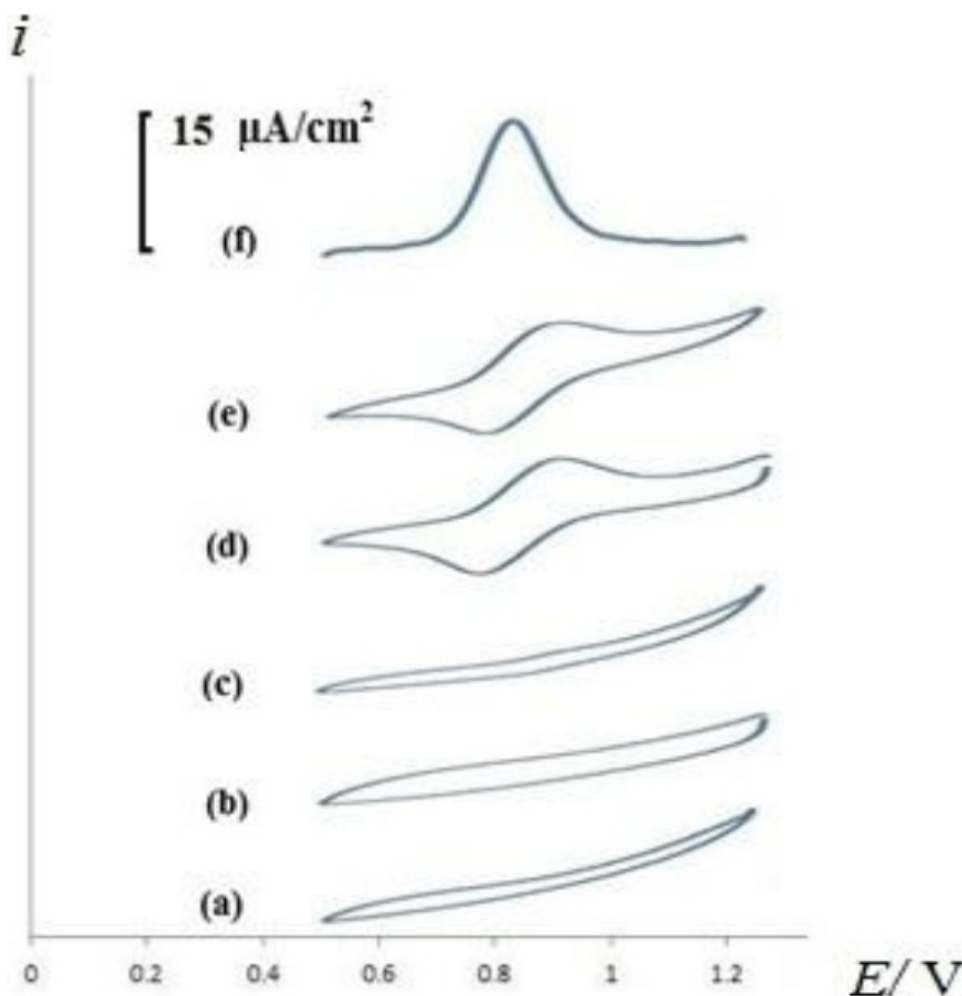

Figure 2 : Cyclic voltammetry CV and differential-pulse voltammetry DPV in 0.1 mol.L^{-1} acetate buffer (pH 4.5) of Nafion-1,10-phenanthroline-modified carbon paste electrode (CMCPE): a) CV without preconcentration potential; b) CV following preconcentration potential; c) CV without preconcentration potential and [Fe^{2+}] = 50 µmol.L^{-1}; d) CV following preconcentration potential with [Fe^{2+}] = 50 µmol.L^{-1}; e) CV following the preconcentration potential with [Fe^{2+}] = 50 µmol.L^{-1}, the voltammogram was recorded between 0.5 V and 1.3 V; f) DPV following the preconcentration potential with [Fe^{2+}] = 50 µmol.L^{-1}, (preconcentration potential: 1.3 V; preconcentration time: 4 min; electrode rotation: 1000 rpm).

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Figure 2f shows the differential-pulse voltammetric response of the reduction process following a potential preconcentration of 1.3 V at the CMCPE for 4 minutes. We obtain a better resolved voltammetric peak which is suitable for quantitative determination of the examined iron(II) in the aqueous solution.

Figure 3 displays the cyclic voltammetry of the CMCPE following a preconcentration potential of 1.3 V for 4 minutes, at various scan rates (from 5 to 100 mV.s^{-1}) in the supporting electrolyte 0.1 mol.L^{-1} acetate buffer (pH 4.5) containing the examined iron(II) ion. The electrochemical data listed in TABLE 1 include the anodic and cathodic peak currents, $I_{p,a}$ and $I_{p,c}$ respectively, the anodic and cathodic peak potentials, $E_{p,a}$ and $E_{p,c}$ respectively, the ratio of anodic to cathodic peak currents ($|I_{p,a}/I_{p,c}|$), the peak to peak potential separations (ΔEp). We found that the values of $E_{p,a}$ and $E_{p,c}$ were independent of the scan rate,

with a mean value of the redox potential calculated to be 851 mV vs Eref, in agreement with the redox potential of ferroïn (Fe(phen)$_3$$^{3+}$/Fe(phen)$_3$$^{2+}$, $E° = 1.06$ V / NHE = 0.86 V / Eref) and the formation constants of the complexes. For all scan rates the values of $I_{p,a}/I_{p,c}$ were close to unity as for a reversible electrochemical system. The difference ΔE_p in anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) peak potentials had a mean value around 125 mV, suggesting charge-transfer limitations at the carbon paste interface[3]. By contrast to surface electrochemical process where the current is linearly related to the potential scan rate, we found that the reduction peak current increased linearly with the square root of the potential scan rate between 5 and 100 mV.s^{-1} (inserted graph in Figure 3) as for a process controlled by diffusion. It can be attributed to the free motion of the accumulated complex in the microenvironment of the CMCPE.

TABLE 1 : Cyclic voltammetric data in 0.1 mol.L^{-1} acetate buffer (pH 4.5) of CMCPE following a preconcentration potential ([Fe^{2+}] = 50 µmol.L^{-1}; preconcentration potential: 1.3 V; preconcentration time: 4 min; electrode rotation: 1000 rpm).

v (mV/s)	$I_{p,c}$ (µA/cm^2)	$E_{p,c}$ (mV)	$I_{p,a}$ (µA/cm^2)	$E_{p,a}$ (mV)	ΔEp (mV)	E° (mV)	$I_{p,a}/I_{p,c}$	$I_{p,c}/I_{p,a}$
5	0.98	790	0.92	917	127	853	0.94	1.06
15	3.00	789	2.59	907	118	848	0.86	1.15
25	4.60	788	3.80	914	126	851	0.81	1.20
50	8.20	788	8.37	916	128	852	1.02	0.97
100	11.90	788	11.92	914	126	851	1.00	0.99

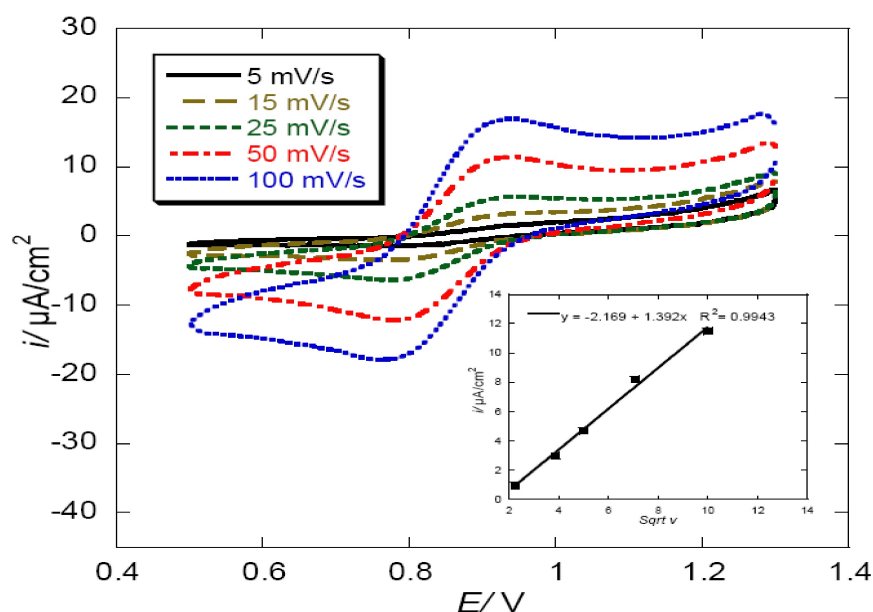$\Delta Ep = | E_{p,a} - E_{p,c}|$; $E° = ½ (E_{p,a} + E_{p,c})$.

Figure 3 : Cyclic voltammetry in the supporting electrolyte 0.1 mol.L^{-1} acetate buffer (pH 4.5) of CMCPE at various scan rates following a preconcentration potential, scan rate varying from 5 to 100 mV.s^{-1}; inserted graph in lower right corner shows the relation between the peak current values obtained from the voltammograms and the square root of the scan rates ([Fe^{2+}] = 50 µmol.L^{-1}; preconcentration potential: 1.3 V; preconcentration time: 4 min; electrode rotation: 1000 rpm).

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Optimum conditions for electrochemical determination of iron(II)

(a) Influence of the supporting electrolyte and pH dependence

Differential-pulse voltammograms of a solution containing 5×10^{-5} mol.L^{-1} of the examined iron(II) were recorded in various supporting electrolytes following a preconcentration potential applied at the CMCPE. The results obtained are listed in TABLE 2. The most intense peak current was obtained in the acetate buffer of pH 4.5 (NaOAc/AcOH). We investigated the pH dependence on the acetate buffer (Figure 4). The peak current increased from pH 2 to pH 4, a maximum peak current height being observed with a pH value between 4 and 4.5, then the peak current decreased at higher pH values. This decrease at higher pH values may be attributed to the precipitation of iron(II) hydroxide. Therefore, a pH value of 4.5 has been chosen for the rest of our investigations.

(b) Differential-pulse parameters

Differential-pulse parameters (scan increment ΔE and pulse amplitude a, duration θ) were optimized to obtain intense and well-defined peaks. We found that the following parameters were suitable for differential-pulse iron(II) determination: $\Delta E = 60$ mV; $a = 1$ mV, $\theta = 20$ ms.

(c) Influence of the preconcentration conditions (potential and time)

Differential-pulse voltammograms of a solution containing 5×10^{-6} mol.L^{-1} of the examined iron(II) in the acetate buffer (pH 4.5) were recorded, under the optimized pulse-parameters, at various preconcentration potentials (Figure 5). As shown in Figure 5, a better and enhanced peak current was achieved at +1.3 V. Therefore, a preconcentration potential of +1.3 V vs Eref was used throughout the present work.

Various preconcentration times were also tested in our study. As shown in Figure 6, the peak current increased linearly with preconcentration time over the range 0-1 minute. In the range 1-6 minutes, the peak current was no longer linear, but a maximum was

TABLE 2 : Influence of the supporting electrolyte on the differential-pulse determination DPV of iron(II) *([Fe^{2+}] = 50 μmol.L^{-1}; preconcentration potential: 1.3 V; preconcentration time: 4 min; electrode rotation: 1000 rpm).*

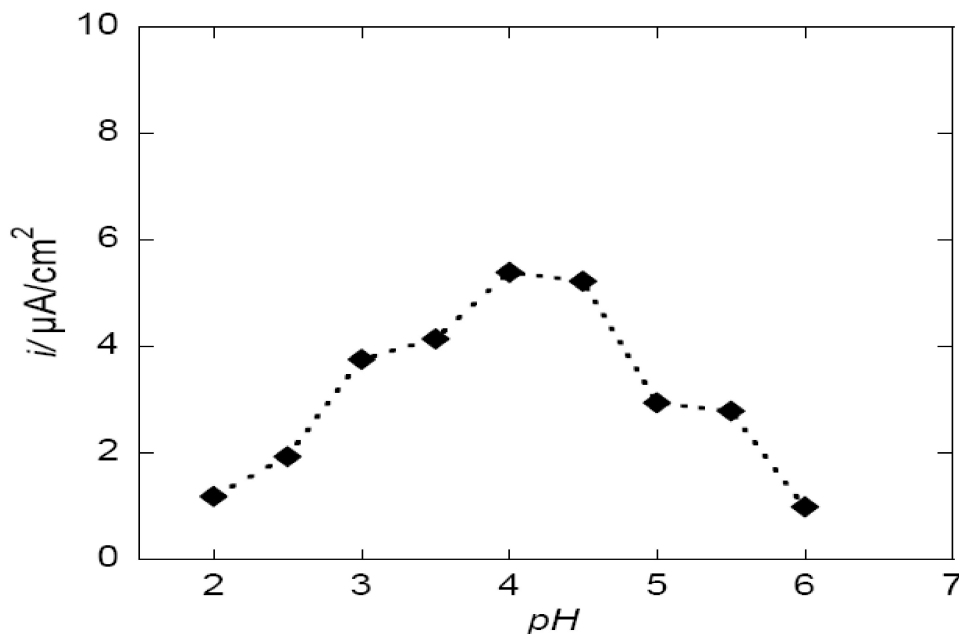| Supporting Electrolyte	Peak current height (μA)	Potential of the peak current (V)
HClO$_4$ (0.1 mol.L^{-1})	2.61	0.94
H$_2$SO$_4$ (0.01 mol.L^{-1})	1.04	0.91
HNO$_3$ (0.1 mol.L^{-1})	1.90	0.92
KCl (0.1 mol.L^{-1})	0.75	0.90
NaOAc/AcOH 0.1 mol.L^{-1} (pH 4.5)	5.23	0.90
NaOH (0.1 mol.L^{-1})	0	0

Figure 4 : Influence of the pH on the differential-pulse determination of iron(II) *([Fe^{2+}] = 50 μmol.L^{-1}; preconcentration potential: 1.3 V; preconcentration time: 4 min; electrode rotation: 1000 rpm).*
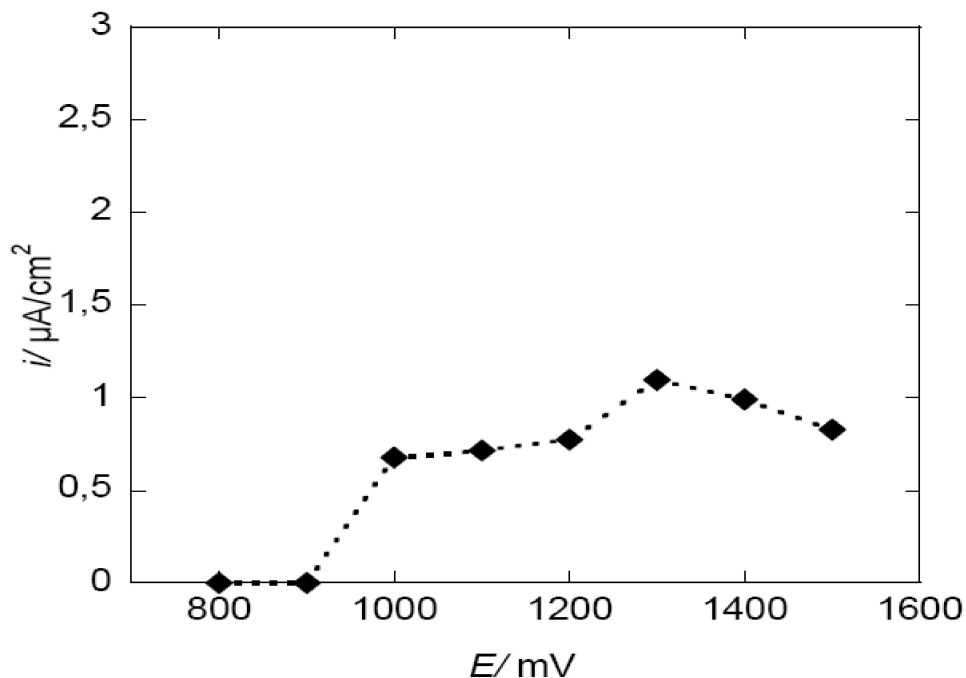
Figure 5 : Influence of the preconcentration potential on the peak current in 0.1 mol.L^{-1} acetate buffer (pH 4.5), ([Fe^{2+}] = 5 μmol.L^{-1}; preconcentration time: 4 min; electrode rotation: 1000 rpm).
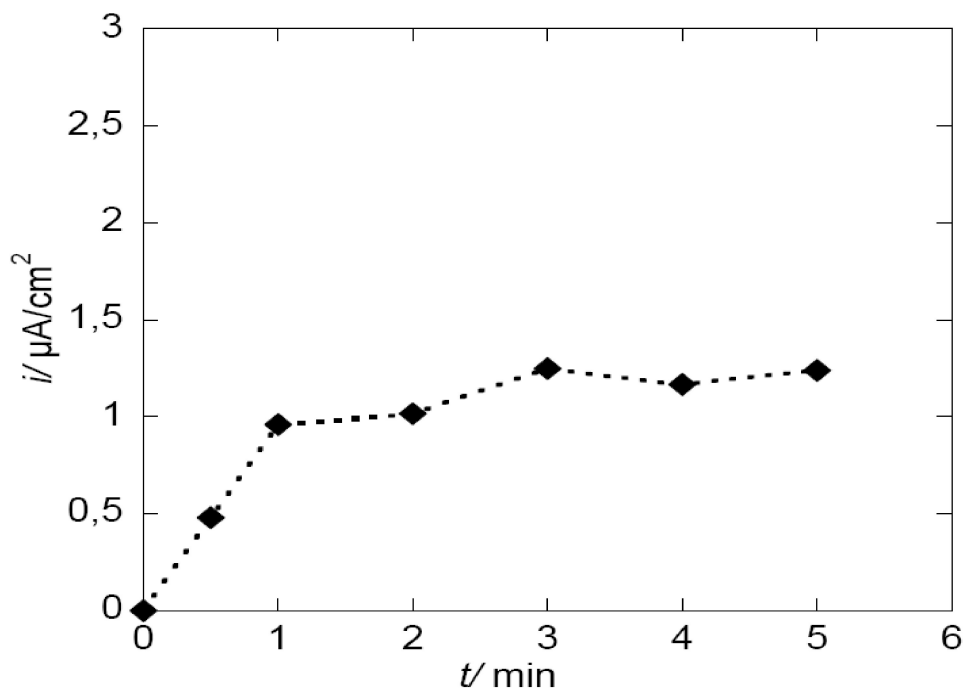

Figure 6 : Influence of the preconcentration time on the peak current in 0.1 mol.L^{-1} acetate buffer (pH 4.5), ([Fe^{2+}] = 5 μmol.L^{-1}; preconcentration potential: 1.3 V; electrode rotation: 1000 rpm).

achieved at a 3 minute preconcentration time. There-fore, we keep this preconcentration time for the rest of our analytical applications.

(d) Surface studies

Surfaces studies were undertaken better to under-stand the morphology of the chemically modified car-bon paste electrode surface and to correlate it with the optimal analytical parameters for differential iron(II) de-termination. This correlation may be of great interest when establishing the performance of the electrochemi-cal sensor.
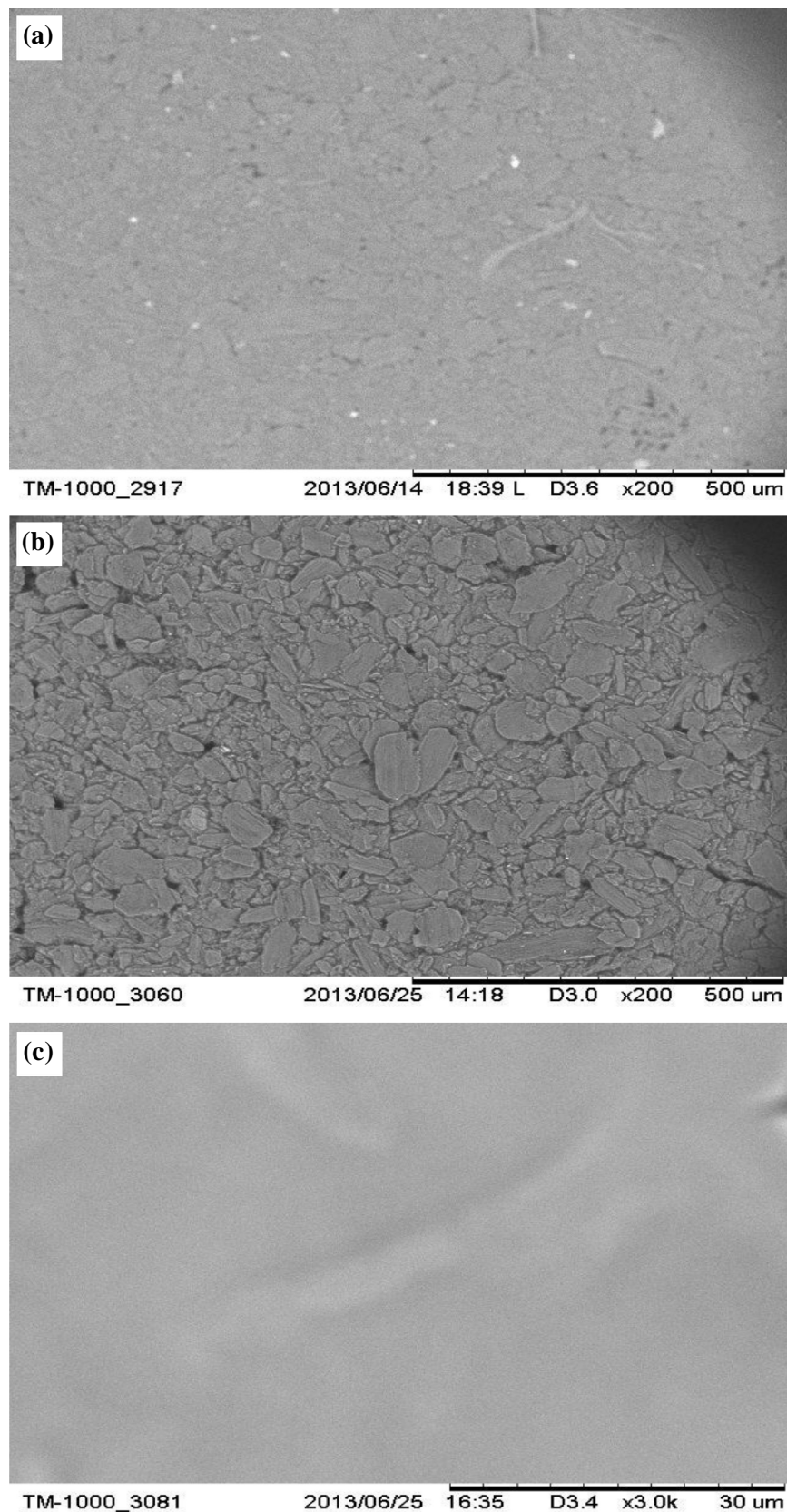
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Figure 7 : Scanning electron microscopic images of (a) bare carbon paste electrode, (b) 1,10-phenanthroline-modified carbon paste electrode, (c) Nafion -1,10-phenanthroline-modified carbon paste electrode (Nafion was coated at the electrode surface by a spin-coating technique).

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Figure 7 shows the SEM image of a bare carbon paste electrode (Figure 7a), the 1,10-phenanthroline-modified carbon paste electrode (Figure 7b) and the Nafion -1,10-phenanthroline-modified carbon paste electrode (Figure 7c).

The bare carbon paste in Figure 7a, before the incorporation of 1,10-phenanthroline, exhibits a porous surface. Results of chemical composition analysis performed by EDX show neither trace of iron nor any foreign metal elements (TABLE 3). After incorporation of 1,10-phenanthroline, the surface becomes rough with the presence of small plates ranging from 7.6 to 91 μm in diameter (Figure 7b). Chemical composition analysis does not reveal the presence of iron or any foreign metal elements (TABLE 3). In contrast, the surface morphology of the Nafion -1,10-phenanthroline-modified carbon paste electrode (Figure 7c) reveals a great difference compared with the bare or 1,10-phenanthroline-modified carbon paste electrode (Figure 7a and 7b). The surface in Figure 7c appears smoother and the small plates which were observed in Figure 7b are no longer visible. Once again, chemical composition analysis does not reveal the presence of iron or any foreign metal elements (TABLE 3).

In the recommended analytical procedure, after immersing the electrode surface into the measuring electrochemical cell, a potential is applied to the electrode under rotation of the rotating disk electrode. Selecting a preconcentration time of 3 minutes, various potential (+1.0 V, 1.3 V and 1.5 V vs Eref) were applied at the CMCPE immersed in the supporting electrolyte 0.1 mol.L^{-1} acetate buffer (pH 4.5) containing the examined iron(II). We investigated first low concentrations of iron(II), varying from $10^{-6} – 10^{-4}$ mol.L^{-1}. In all cases, the level of incorporated iron in the CMCPE was under the EDX detection level. In the case of an iron(II) concentration of 10^{-3} mol.L^{-1}, we obtain the SEM images Figures 8a, 8b and 8c corresponding to the applied potentials 1.0 V, 1.3 V and 1.5 V respectively. While the surfaces remain smoother (with the presence of dark marks) for applied potentials of 1.0 V (Figure 8a) and 1.3 V (Figure 8b), the surface becomes rougher with a lot of crackles and surface defects for an applied potential of 1.5 V (Figure 8c). Moreover, chemical composition analysis (TABLE 3) shows that the iron content increases from 21.6 % to 61.3 %, with increasing applied potentials from 1.0 V to 1.3 V. Noting that the maximum current was achieved for an applied preconcentration potential of 1.3 V (Figure 5), this potential could be understood as the optimal preconcentration potential which allows a maximum iron complex incorporation into the Nafion-coated electrode. For higher applied preconcentration potentials, we notice a decrease of iron content at the electrode surface. At an applied potential of 1.5 V, we even notice a lack of iron at some portion of the chemically modified carbon paste electrode. The process of accumulation into the Nafion-coated surface does not occur properly, due to higher residual current and surface processes at the carbon paste that induces a rougher and a crackled surface. At 1.5 V on a carbon electrode, it is the beginning of the solvent discharge which modifies the structure of the carbon paste. This is supported by the voltammogram in Figure 2, which shows a stable and low residual current over the range 0.0 to +1.3 V. For potentials greater than 1.3 V, the background current increases. This may explain why the peak current decreases at higher potentials as seen in Figure 5.

TABLE 3 : Results of chemical composition analysis of various CMCPE surfaces.

System	Elements (%)		
	Fe	F	S
Bare carbon paste electrode	-	-	-
1,10-phenanthroline-modified carbon paste electrode	-	-	-
Nafion -1,10-phenanthroline-modified carbon paste electrode	-	-	100
Nafion -1,10-phenanthroline-modified carbon paste electrode after an applied potential of 1.0 V vs Eref*	21.6	49.7	28.7
Nafion -1,10-phenanthroline-modified carbon paste electrode after an applied potential of 1.3 V vs Eref*	61.3	-	38.7
Nafion -1,10-phenanthroline-modified carbon paste electrode after an applied potential of 1.5 V vs Eref*	-	70	30

*Preconcentration time: 3 minutes, electrolyte 0.1 mol.L^{-} acetate buffer (pH 4.5) containing 10^{-3} mol.L^{-1} Fe (II), electrode rotation: 1000 rpm.
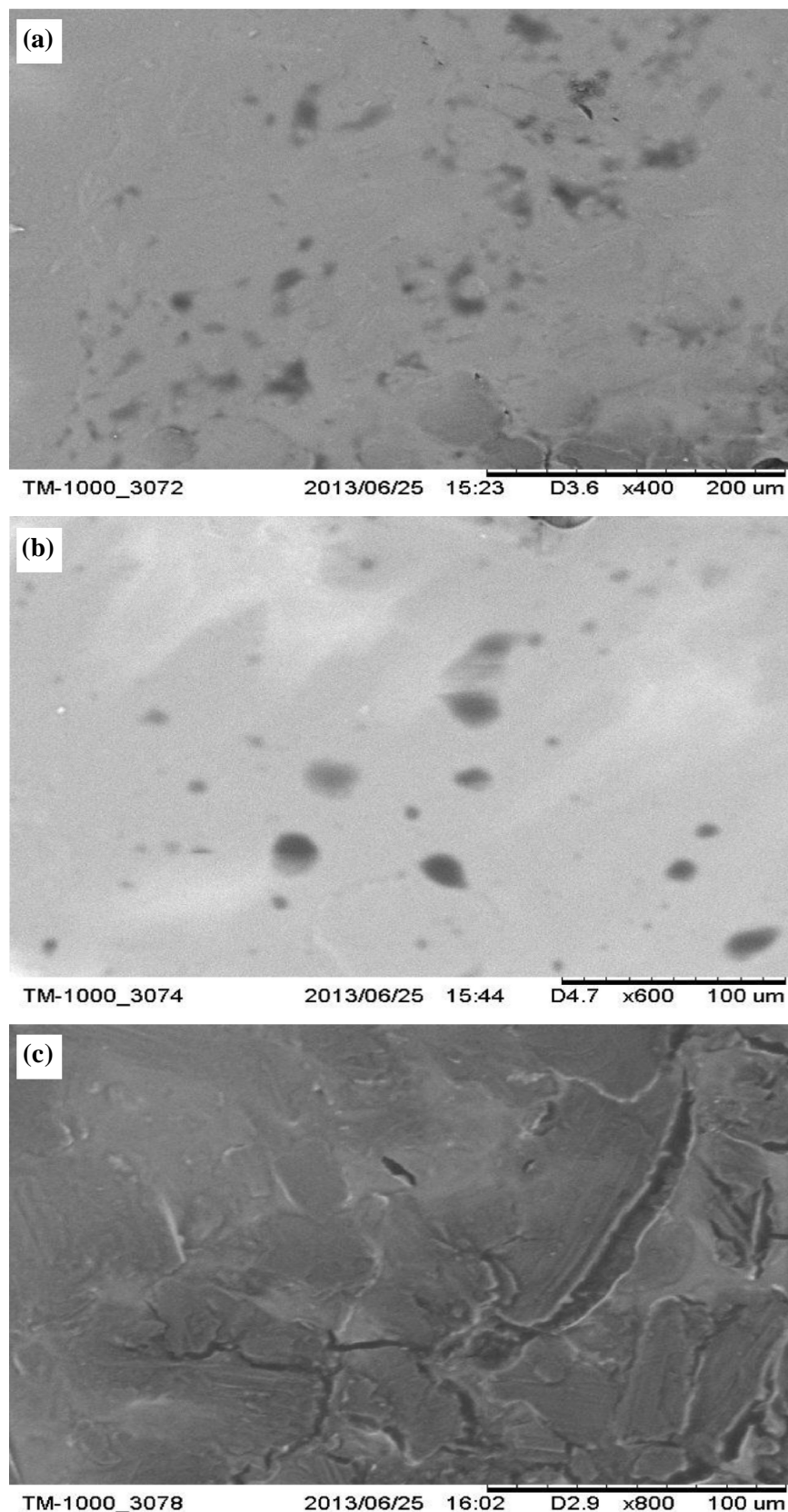
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Figure 8 : Scanning electron microscopic images of a Nafion -1,10-phenanthroline-modified carbon paste electrode after an applied potential of (a) 1.0 V, (b) 1.3 V and (c) 1.5 V. ([Fe^{2+}] = 1 mmol.L^{-1}; supporting electrolyte 0.1 mol.L^{-1} acetate buffer (pH 4.5); preconcentration time: 3 min; electrode rotation: 1000 rpm).

Impedance measurements

To better understand the features of the CMCPE corresponding to various preconcentration potentials applied at the electrode immersed in the supporting electrolyte (10^{-5} mol.L^{-1} Fe^{2+} in 0.1 mol.L^{-1} of an acetate buffer pH 4.5), electrochemical impedance spectroscopy experiments were carried out at open circuit potential under a pure diffusion regime. The Nyquist plots are displayed in Figure 9.

At first, according to a simple Randles scheme, the Nyquist plot of the CMCPE shows a straight line (Figure 9a), which is a constant phase element behavior with a huge resistor. The high resistance reflects that with no iron(II) there is no charge transfer at the electrodes. After the preconcentration process, the recorded Nyquist plots (Figure 9b, c and d) are no more linear, but include at higher frequencies a semicircle portion lying on the real-axis followed by a straight line. It is seen from Figure 9 that the smallest semicircle portion was achieved in the case where the applied preconcentration potential was 1.3 V. A charge transfer resistance (Figure 9c) of around 3000 Ω is evaluated by the estimated diameter of the semicircle; this is

in agreement with a high concentration of the redox couple. A preconcentration potential of 1 V leads to a charge transfer resistance (Figure 9b) of around 1.1 10^4 Ω; this potential is insufficient to yield a convenient concentration of the redox couple. The largest semicircle region was obtained for a preconconcentration potential of 1.5 V, the evaluated charge transfer resistance (Figure 9d) is around 2 10^4 Ω. While the preconcentration should accumulate the redox couple, the destructuration effect observed by the SEM images prevents the charge transfer to proceed: although the iron complex concentration should increase, the charge transfer resistance increases.

In fact, the Randles model was found inappropriate when simulations were carried out on the impedance results. For high frequencies, two overlapping time constants could be deduced for charge transfer and ionic conduction (see Figure 9d); for low frequencies, mass transfer controlled the quasi-linear part of the diagram. For the data analysis of impedance spectra, we used the model of Figure 10a, previously reported[54], which is a modified model of painted metal electrode. R$_s$ is as usual the ohmic resistance of the electrolyte between
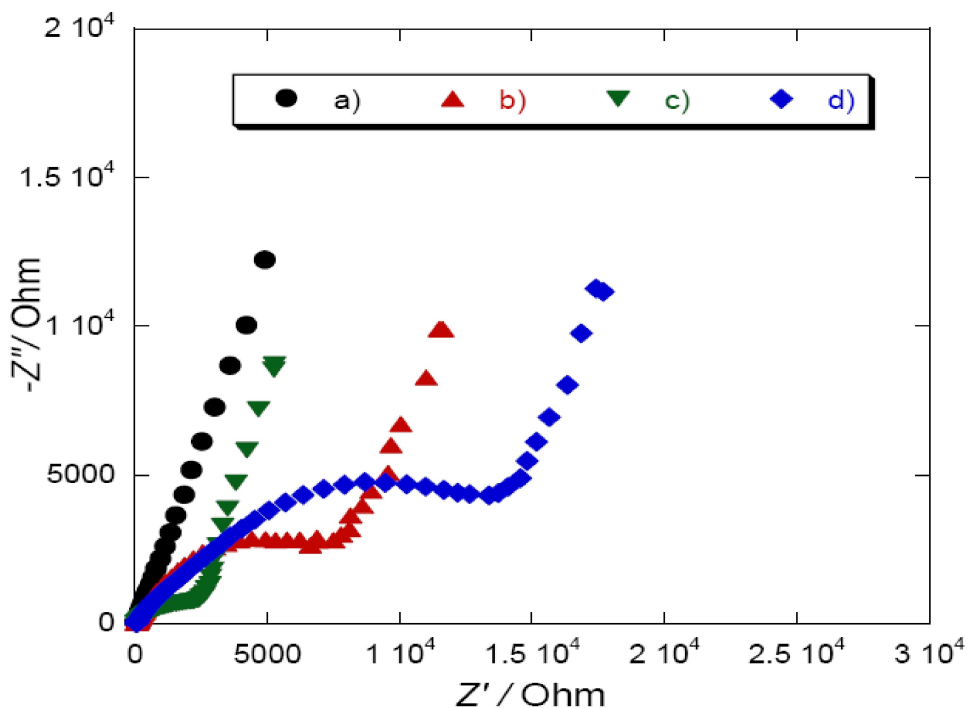

Figure 9 : Nyquist plots of the CMCPE in the supporting electrolyte (10^{-5} mol.L^{-1} Fe^{2+} in 0.1 mol.L^{-1} acetate buffer pH 4.5). Various preconcentration potentials were applied at the CMCPE immersed in the solution before recording the Nyquist plots at open circuit potential: a) CMCPE without prior preconcentration potential and immersed in 0.1 mol.L^{-1} acetate buffer pH 4.5; b) CMCPE after a preconcentration potential of 1 V; c) CMCPE after a preconcentration potential of 1.3 V; d) CMCPE after a preconcentration potential of 1.5 V.

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the working and reference electrodes; R_f and Q_f characterize the ohmic resistance and the imperfect capacitance of the film, a dielectric component; Q_{dl} is an imperfect capacitance of the double layer of the electrode interface: carbon grains/solute; the mass transport of the redox couple towards the electrode is represented by a constant phase element Q and a mass transfer resistance Z which replace the classic Warburg impedance[54]. The experimental data were then fitted to this electronic equivalent circuit shown in Figure 10a. Selected data are listed in TABLE 4. As expected the electrolyte resistance R_s is of the same order of magnitude around 45-50 Ω. It can be noticed that the film resistance R_f depends on the potential preconcentration: R_f increases as the potential. The film is an ion exchange polymer, sulfonate ions RSO_3^- constitute the skeleton, and the conductivity of the film is related to the mobile ions Na^+ or Fe^{2+}. Under a potential of 1 V, there is no accumulation and Na^+ ions control the conductivity.

Under a potential of 1.3 V, Na^+ has been exchanged by Fe^{2+} and the conductivity decreases or R_f increases. Finally, under a potential of 1.5 V, the huge increase of R_f may be explained by the destruction of the film. As concerns the electrochemical process, under the preconcentration potential of 1.3 V corresponding to the highest redox couple concentration, the double layer capacitance is maximum and the charge transfer resistance is minimum. Concerning the mass transport, the product $Q \times Z$ corresponds to a time constant for the mass transport; it can be noticed that this time constant is the lowest under 1.3 V because a high concentration of iron complex is present. Figure 10b represents a scheme of charge transfers at the Nafion - 1,10-phenanthroline-modified carbon paste electrode. During accumulation, the film behaves as an ion exchange resin between Fe^{2+} and Na^+; then Fe^{2+} is complexed by 1,10-phenanthroline and readily oxidized into Fe^{III}, Na^+ ions migrate towards the solution.
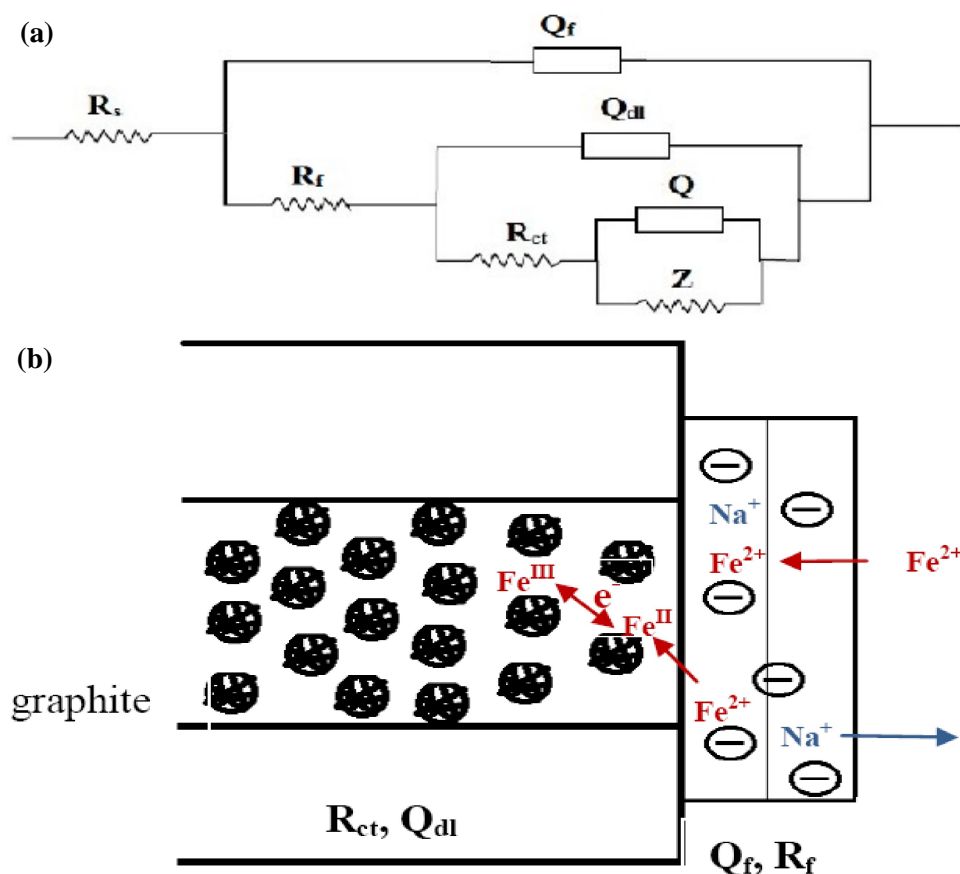

Figure 10 : a) Electronic equivalent circuit of the CMCPE immersed in the supporting electrolyte: solution resistance R_s, resistance and imperfect capacitance of the film R_f and Q_f, charge transfer resistance and imperfect double-layer capacitance R_{ct} and Q_{dl}, mass transport parameters Q and Z; b) Scheme of charges transfer at the Nafion -1,10-phenanthroline-modified carbon paste electrode: $\ominus$ represents the charge of the Nafion RSO_3^- skeleton, $Fe^{II} = Fe(phen)_3^{2+}$, $Fe^{III} = Fe(phen)_3^{3+}$.

TABLE 4 : Selected fitted data of electrochemical impedance values obtained from Figure 9

Sample	R_s (Ω)	R_f (Ω)	Q_{dl} (µF) / n	R_{ct} (Ω)	Q (mF) / n	Z (Ω)
+ 1 V	48.5	111	30.6 / 0.66	9570	1.03 / 0.9	5.6×10^4
+ 1.3 V	43.4	354	54.2 / 0.55	4260	0.57 / 0.85	9.2×10^4
+ 1.5 V	50.4	6830	21.8 / 0.82	9789	0.95 / 0.89	9.7×10^4

Once the accumulation process has taken place, the electrochemical process occurred at the carbon grain boundaries on the Fe^{III}/Fe^{II} redox couple. According to the proposed scheme, the mass transport occurred in the carbon paste: diffusion of the iron complex with the migration of Na^+ ions. Under a potential of 1.3 V, the high concentration of iron explains the low time constant and the increase of Z because Na^+ concentration decreases. Under a potential of 1.5 V, the electrode is denatured.

The impedance results are in good agreement with the previous results in this work: in the case of a preconcentration potential of +1.3 V, a better and enhanced peak current for the differential-pulse voltammetric determination of iron(II) was achieved (Figure 5) and as shown in TABLE 3 the iron content

at the electrode surface was maximum; SEM images revealed that at potentials greater than 1.3 V a rougher and crackled surface appeared (Figure 8).

Analytical applications

Before applying an analytical procedure to real samples, one must be careful to assess the performance of the electrochemical sensor. The sensor linear response was verified using the calibration plot of iron(II) in acetate buffer solution (pH 4.5). Figure 11 shows differential-pulse stripping voltammograms for solutions of increasing iron(II) concentration, $10^{-7} - 1.6 \times 10^{-6}$ mol.L^{-1}. Well-defined peaks, which increase linearly with the iron(II) concentration, are observed. The calibration plot is also shown in Figure 11 (inserted graph). A linear dependence of stripping signal on increasing concentration of iron(II) is obtained with a correlation coefficient R^2 equals 0.9989.

The following relation was used to calculate the limit of detection (*LOD*)[55]:

$$LOD = \frac{k\, S_{y/x}}{a}$$

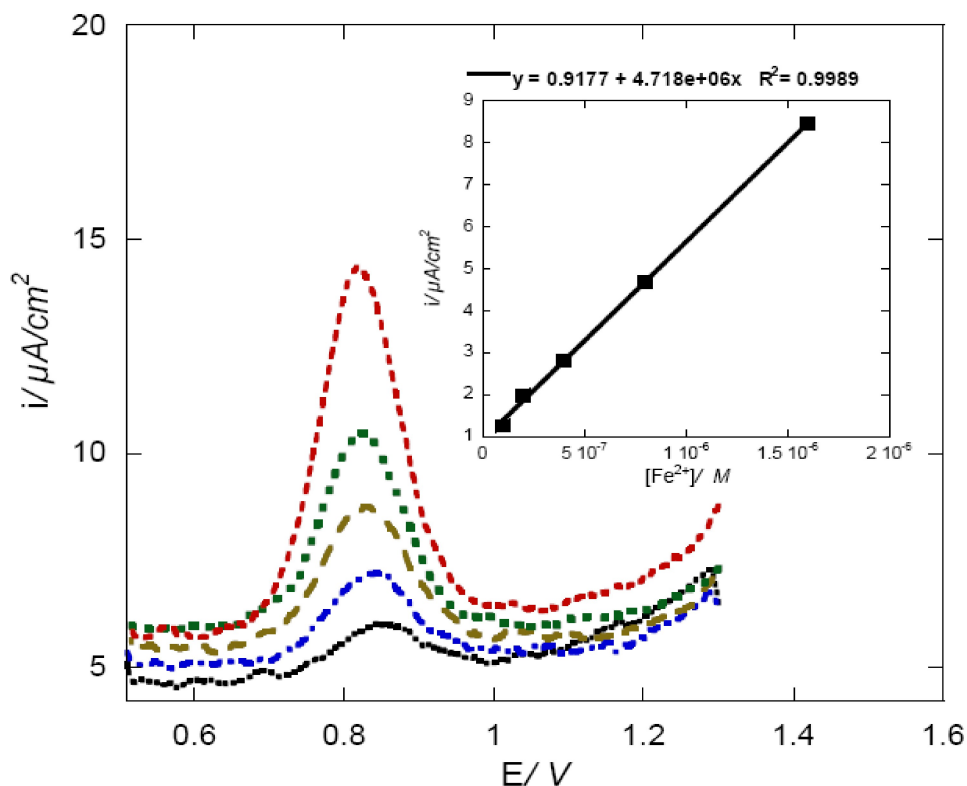where $S_{y/x}$ is the standard deviation, and *a* is the slope

Figure 11 : Differential-pulse stripping DPV voltammograms for solutions of increasing iron(II) concentration, $10^{-7} - 1.6 \times 10^{-6}$ mol.L^{-1}. Inserted graph in upper right corner shows the calibration plot over the range $10^{-7} - 1.6 \times 10^{-6}$ mol.L^{-1}, (preconcentration potential: 1.3V for 3 minutes, electrode rotation: 1000 rpm, 0.1 mol.L^{-1} acetate buffer pH 4.5)

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of the calibration plot, and k is a constant equal to 3 as recommended by IUPAC[56]. The standard deviation was $S_{y/x} = 0.056$ and $a = 4.7 \times 10^6$, leading to the limit of detection of 3.6×10^{-8} mol.L^{-1} (0.00202 mg/L).

We estimated the accuracy by analyzing a certified solution of iron(II) (0.1 mg/L) using the standard addition method. A recovery of 99.01 % was obtained. The relative standard deviation (precision of the method) for five determinations of 1×10^{-6} mol.L^{-1} iron(II) was 1.5 %. The results are very satisfactory and indicate that the proposed method can be used for iron(II) determination in aqueous samples.

The analytical utility of the sensor has been assessed by application to the determination of iron(II) metal ion in real groundwater samples. The investigated groundwater samples were collected in a village called Yamtenga (UTM coordinates: X = 669126 and Y = 1363944) located at the outskirts of Ougadougou (Figure 1 given

in supplementary information). The samples were collected at 11 groundwater sites (TABLE 5).

Usually, the water coming from groundwaters can be drunk by local people, and it is full of micro-amount of elements which are needed for human health. Sometimes this water cannot be drunk because it is brown and grey, and it smells. This color is generally connected to the presence of iron(II) and manganese(II) metal ions in groundwater. People then complain about the quality of the groundwaters they drink. The results of real determination of iron(II) metal ions in groundwater samples from this village are given in TABLE 6. The iron(II) metal ion concentration profiles obtained from the collected groundwater samples sites of TABLE 5 are shown in Figure 12. The results indicate that the iron contents of the sites are higher than the admitted guideline value (0.3 mg/L) in drinking water given by the WHO for human consumption. Groundwater is water which is situated in underground aquifers. It is known that in the aquifer zone, which can consist of several hydraulically separated zones, the final composition of the groundwater is influenced through contact with the solid rock matrix. Therefore a first source of heavy metal ions in groundwater could be their release in the aquifer when water comes into contact with areas of the solid rock matrix. Another source can be the release of heavy metal ions from anthropogenic activities and their transportation through rivers and streams as either dissolved species in water or as an integral part of suspended sediments; they may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources, particularly wells. In the present case, only the second source

TABLE 5 : Location of groundwater samples sites in the village of Yamtenga.

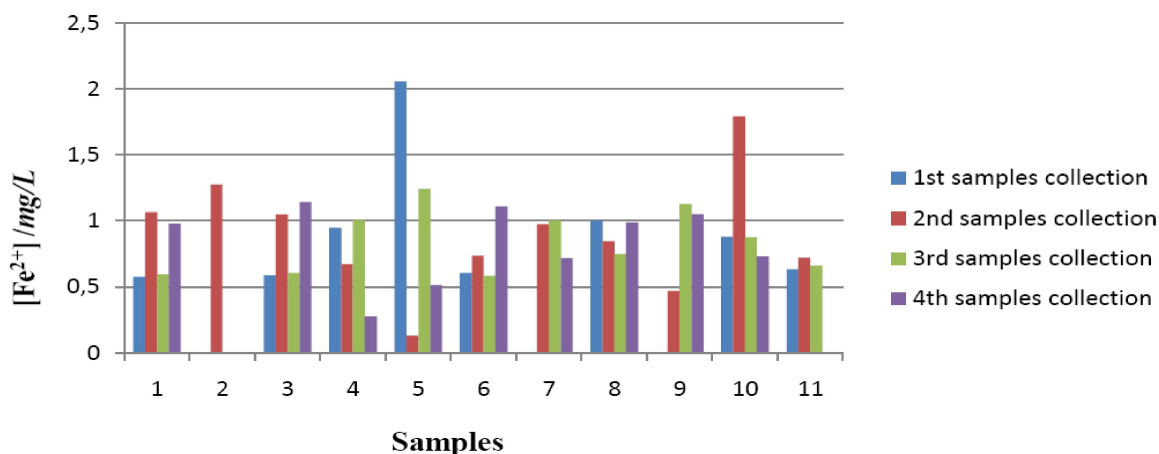| Groundwater samples sites	XUTM	YUTM	Longitude	Latitude
1	668608	1364016	1° 26' 57.74"	12° 20' 3.753"
2	668700	1364264	1° 26' 54.64"	12° 20' 11.80"
3	668914	1364466	1° 26' 47.52"	12° 20' 18.33"
4	663124	1389698	1° 26' 28.40"	12° 34' 5.61"
5	667573	1364658	1° 27' 31.78"	12° 20' 24.83"
6	667562	1364135	1° 27' 32.33"	12° 20' 7.82"
7	667770	1364890	1° 27' 25.31"	12° 20' 32.35"
8	667926	1364370	1°27' 20.40"	12° 20' 15.40"
9	667804	1365541	1° 27' 24.06"	12° 20' 53.53"
10	668403	1365389	1° 27' 4.26"	12° 20' 48.47"
11	669023	1365095	1° 26' 43.79"	12° 20' 38.78"

Figure 12 : Iron(II) metal ion profiles concentration obtained from the collected sites of TABLE 5.

of pollution will be used to explain the high content of iron(II) metal ions. The first one is improbable because the geological map (Figure 2 given in supplementary information) has shown that iron is not a major constituent of the area and could not enter the aquifer by dissolution of rock and soil.

TABLE 6 : Determination of iron(II) from real groundwaters samples by the standard addition method. The iron(II) contents are expressed in mg/L.

Groundwater samples	1st samples collection (06 November 2010)	2nd samples collection (06 February 2011)	3rd samples collection (30 July 2011)	4th samples collection (22 October 2011)
1	0.576	1.068	0.594	0.98
2	-	1.276	-	-
3	0.586	1.046	0.606	1.142
4	0.948	0.672	1.006	0.276
5	2.06	0.132	1.244	0.514
6	0.606	0.736	0.582	1.11
7	-	0.976	1.002	0.718
8	1.002	0.848	0.748	0.99
9	-	0.47	1.13	1.052
10	0.88	1.792	0.876	0.73
11	0.634	0.722	0.662	-

CONCLUSION

Differential pulse voltammetric determination of iron(II) using Nafion-1,10-phenanthroline-modified electrode has been studied. Optimal analytical parameters for iron(II) determination have been ascertained. SEM image corresponding to a maximum recovery of the examined iron(II) ion, chemical composition analysis and impedance measurements were in good agreement with the preconcentration potential of +1.3 V vs Eref used for the accumulation/differential pulse voltammetric determination of iron(II) at the Nafion-1,10-phenanthroline-modified carbon paste electrode. Assuming a simple model based on a redox polymer-modified electrode, the impedance measurements showed that the lowest charge transfer resistance could be achieved for a preconcentration potential of +1.3 V vs Eref applied at the CMCPE immersed in a supporting electrolyte containing the acetate buffer pH 4.5 and the examined iron(II) ion.

The performance of the electrochemical sensor was verified by analyzing a reference standard solution of iron(II). The results, estimated as recovery and standard deviation, were satisfactory. Real groundwaters samples were also analyzed in a village by the standard addition method. Determination of other heavy metals ions are under investigation in our laboratory. The present data constitute the first study on iron(II) contaminated groundwaters in Burkina Faso and will be extended to others rural environment where heavy metals ions pollution (Cu^{2+}, Tl^{+}, Mn^{2+} and Fe^{2+}) has been detected. The next step of our work will be the implementation of an adsorption column for the removal of these ions from groundwaters in rural environment.

ACKNOWLEDGEMENTS

REFERENCES

[1] M.Esteban, E.Casassas; Stripping electroanalytical techniques in environmental analysis, Trends in Anal.Chem., **13(3)**, 110 (**1994**).

[2] Z.Gao, P.Li, G.Wang, Z.Zhao; Preconcentration and differential-pulse voltammetric determination of iron(II) with Nafion-1,10-phenanthroline-modified carbon paste electrodes, Anal.Chim.Acta, **241(1)**, 137 (**1990**).

[3] Z.Gao, P.Li, Z.Zhao; Determination of iron(II) with chemically-modified carbon paste electrodes, Talanta, **38(10)**, 1177 (**1991**).

[4] Imane Adraoui, Aziz Amine; Détermination des métaux lourds par voie électrochimique, Les Technologies de Laboratoire, **2(4)**, 16 (**2007**).

[5] E.Czop, A.Economou, A.Bobrowski; A study of in situ plated tin-film electrode for the determination of trace metals by means of square-wave anodic stripping voltammetry, Electrochim.Acta, **56(5)**, 2206 (**2011**).

ORIGINAL ARTICLE

[6] E.M.Ghoneim; Simultaneous determination of Mn(II), Cu(II) and Fe(III) as 2-(52 -bromo-22 -pyridylazo)-5-diethylaminophenol complexes by adsorptive cathodic stripping voltammetry at a carbon paste electrode, Talanta, **82(2)**, 646 **(2010)**.

[7] B.S.Sherigara, Y.Shivaraj, R.J.Mascarenhas, A.K.Satpati; Simultaneous determination of lead, copper and cadmium onto mercury film supported on wax impregnated carbon paste electrode: Assessment of quantification procedures by anodic stripping voltammetry, Electrochim.Acta, **52(9)**, 3137 **(2007)**.

[8] J.Wang; Stripping Analysis: Principles, Instrumentation and Applications, VCH Publishers, Deerfield Beach, Florida, 160 **(1985)**.

[9] N.Abo El-Maali, Y.M.Temerk, M.Sh-Abd El-Aziz; Application of stripping voltammetry at a static mercury drop electrode for the determination of aluminium and iron in Portland cement, Anal.Chim. Acta, **353(2-3)**, 313 **(1997)**.

[10] J.Zhao, W.Jin; A study on the adsorption voltammetry of the iron(III)-2-(52 -bromo-22 -pyridylazo)-5-diethylaminophenol system, J.Electroanal.Chem., **267(1-2)**, 271 **(1989)**.

[11] J.Wang; Analytical Electrochemistry, Third Edition, WILEY-VCH Publishers, United States of America, 250 **(2006)**.

[12] A.Economou, P.R.Fielden; Mercury film electrodes: Developments, trends and potentialities for electroanalysis, Analyst, **128(3)**, 205 **(2003)**.

[13] J.Wang, J.Lu; Adsorptive stripping voltammetry of trace manganese in the presence of 2-(52 -bromo-22 -pyridylazo)-5-diethylaminophenol (5-Br-PADAP), Talanta, **42(3)**, 331 **(1995)**.

[14] S.Tanaka, K.Sugawara, M.Taga; Adsorption voltammetry of the copper (II) 2-(52 -bromo-22 -pyridylazo)-5-diethylaminophenol complex, Talanta, **37(10)**, 1001 **(1990)**.

[15] J.Lu, W.Jin, S.Wang; Adsorption voltammetry of the vanadium-2-(52 -bromo-22 -pyridylazo)-5-diethylaminophenol (5-Br-PADAP) system, Anal.Chim.Acta, **238**, 375 **(1990)**.

[16] M.A.Nolan, S.P.Kounaves; Microfabricated array of Iridium microdisks as a substrate for direct determination of Cu^{2+} or Hg^{2+} using square-wave anodic stripping voltammetry, Anal.Chem., **71(16)**, 3567 **(1999)**.

[17] K.Kalcher, J.-M.Kauffmann, J.Wang, I.Švancara, K.Vytřas, C.Neuhold, Z.Yang; Sensors based on carbon paste in electrochemical analysis: A review with particular emphasis on the period 1990-1993, Electroanal., **7(1)**, 5 **(1995)**.

[18] J.Wang, B.Tian; Mercury-free disposable lead sensors based on potentiometric stripping analysis of gold-coated screen-printed electrodes, Anal.Chem., **65(11)**, 1529 **(1993)**.

[19] J.Wang, J.-M.Lu, S.B.Hocevar, P.A.M.Farias; Bismuth-coated carbon electrodes for anodic stripping voltammetry, Anal.Chem., **72(14)**, 3218 **(2000)**.

[20] S.B.Hocevar, I.Svancara, K.Vytras, B.Ogorevc; Novel electrode for electrochemical stripping analysis based on carbon paste modified with bismuth powder, Electrochim.Acta, **51(4)**, 706 **(2005)**.

[21] E.A.Hutton, B.Ogorevc, S.B.Hocevar, M.R.Smyth; Bismuth film microelectrode for direct voltammetric measurement of trace cobalt and nickel in some simulated and real body fluid samples, Anal.Chim. Acta, **557(1-2)**, 57 **(2006)**.

[22] S.V.Prabhu, R.P.Baldwin; Constant potential amperometric detection of carbohydrates at a copper-based chemically modified electrode, Anal. Chem., **61(8)**, 852 **(1989)**.

[23] S.V.Prabhu, R.P.Baldwin, L.Kryger; Chemical preconcentration and determination of copper at a chemically modified carbon-paste electrode containing 2,9-dimethyl-1,10-phenanthroline, Anal.Chem., **59(8)**, 1074 **(1987)**.

[24] K.N.Thomson, L.Kryger, R.P.Baldwin; Voltammetric determination of traces of nickel(II) with a medium exchange flow system and a chemically modified carbon paste electrode containing dimethylglyoxyme, Anal.Chem., **60(2)**, 151 **(1988)**.

[25] J.Wang, M.Bonakdar; Preconcentration and voltammetric measurement of mercury with a crown-ether modified carbon-paste electrode, Talanta, **35(4)**, 277 **(1988)**.

[26] J.F.Price, R.P.Baldwin; Preconcentration and determination of ferrocenecarboxaldehyde at a chemically modified platinum electrode, Anal.Chem., **52(12)**, 1940 **(1980)**.

[27] K.N.Thomson, R.P.Baldwin; Amperometric detection of nonelectroactive cations in flow systems at a cupric hexacyanoferrate electrode, Anal.Chem., **61(23)**, 2594 **(1989)**.

[28] L.A.Coury, Jr., E.M.Birch, W.R.Heineman; Gamma-irradiated polymer modified-graphite electrodes with enhance response to catechol, Anal. Chem., **60(6)**, 553 **(1988)**.

[29] A.Komersová, M.Bartoš, K.Kalcher, K.Vytřas; Trace iron determination in aminoisophthalic acid

using differential-pulse cathodic stripping voltammetry at carbon paste electrodes, J.Pharm. Biomed.Anal., **16(8)**, 1373 **(1998)**.

[30] R.Segura, M.Inés Toral, V.Arancibia; Determination of iron in water samples by adsorptive stripping voltammetry with a bismuth film electrode in the presence of 1-(2-piridylazo)-2-naphthol, Talanta, **75(4)**, 973 **(2008)**.

[31] R.F.Lane, A.T.Hubbard; Electrochemistry of chemisorbed molecules.I.Reactants connected to electrodes through olefinic substituents, J.Phys.Chem., **77(11)**, 1401 **(1973)**.

[32] P.R.Moses, L.Wier, R.W.Murray; Chemically modified tin oxide electrode, Anal.Chem., **47(12)**, 1882 **(1975)**.

[33] C.Mariame, M.El Rhazi, I.Adraoui; Determination of Traces of Copper by Anodic Stripping voltammetry at a rotating carbon paste disk electrode modified with poly(1,8-diaminonaphtalene), J.Anal.Chem., **64(6)**, 632 **(2009)**.

[34] I.Adraoui, M.El Rhazi, A.Amine, C.Mariame; Applications analytiques des films minces de mercure protégés par du fibrinogène pour la détermination du plomb et du cadmium dans les échantillons d'eaux usées et d'eaux de mer, Afrique SCIENCE, **2(3)**, 263 **(2006)**.

[35] R.J.Mascarenhas, A.K.Satpati, S.Yellapa, B.S.Sherigara; Wax-impregnated carbon paste electrode modified with mercuric oxalate for the simultaneous determination of heavy metal ions in medicinal plants and Ayurvedic tablets, Anal.Sci., **22(6)**, 871 **(2006)**.

[36] S.B.Khoo, S.X.Guo; Rapidly renewable and reproducible electropolymerized surface at a monomer modified carbon paste electrode, J.Electroanal. Chem., **465(1)**, 102 **(1999)**.

[37] S.Majid, M.El Rhazi, A.Amine, A.Currili, G.Palleschi; Carbon paste electrode bulk-modified with the conducting polymer poly(1,8-Diaminonaphathalene): Application to lead determination, Microchim.Acta, **143(2-3)**, 195 **(2003)**.

[38] G.T.Cheek, R.F.Nelson; Applications of chemically modified electrodes to analysis of metal ions, Anal.Lett., **A11(5)**, 393 **(1978)**.

[39] P.Li, Z.Gao, Y.Xu, G.Wang, Z.Zhao; Determination of trace amounts of silver with a chemically modified carbon paste electrode, Anal.Chim.Acta, **229**, 213 **(1990)**.

[40] Kurt Kalcher; Voltammetric determination of trace amounts of gold with a chemically modified carbon paste electrode, Anal.Chim.Acta, **177**, 175 **(1985)**.

[41] Z.Gao, P.Li, S.Dong, Z.Zhao; Voltammetric determination of trace amounts of gold(III) with a carbon paste electrode modified with a chelating resin, Anal.Chim.Acta, **232**, 367 **(1990)**.

[42] P.Hernandez, E.Alda, L.Hernandez; Determination of mercury(II) using a modified electrode with zeolite, Fresenius Zeit.Anal.Chem., **327(7)**, 676 **(1987)**.

[43] L.Hernandez, P.Hernandez, M.H.Blanco, M.Sanchez; Determination of copper(II) with a carbon paste modified with an ion-exchange resin, Analyst (London), **113(1)**, 41 **(1988)**.

[44] C.Hu, K.Wu, X.Dai, S.Hu; Simultaneous determination of lead(II) and cadmium(II) at a diacetyldioxime modified carbon paste electrode by differential pulse stripping voltammetry, Talanta, **60(1)**, 17 **(2003)**.

[45] A.Ferancova, E.Korgova, J.Labuda, J.Zima, J.Barek; Cyclodextrin modified carbon paste based electrodes as sensors for the determination of carcinogenic polycyclic aromatic amines, Electroanal., **14(23)**, 1668 **(2002)**.

[46] D.Savitri, C.K.Mitra; Modeling the surface phenomena in carbon paste electrodes by low frequency impedance and double-layer capacitance measurements, Bioelectroch.Bioenerg., **48(1)**, 163 **(1999)**.

[47] M.Muti, A.Erdem, A.Calishan, A.Sinag, T.Yumak; Electrochemical behavior of carbon paste electrodes enriched with tin oxide nanoparticles using voltammetry and impedance spectroscopy, Colloid Surface B, **86(1)**, 154 **(2011)**.

[48] A.Rodríguez-López, D.Torres, J.Mojica-Gomez, C.Estrada-Artega, R.Antaño- López; Characterization by electrochemical impedance spectroscopy of magnetic nanoparticles supported on carbon paste electrode, Electrochim.Acta, **56(23)**, 8078 **(2011)**.

[49] Ren-Xia Xu, Xin-Yao Yu, Chao Gao, Yu-Jing Jiang, Dong-Dong Han, Jin-Huai Liu, Xing-Jiu Huang; Non-conductive nanomaterial enhanced electrochemical response in stripping voltammetry: The use of nanostructured magnesium silicate hollow spheres for heavy metal ions detection, Anal.Chim. Acta, **790**, 31 **(2013)**.

[50] H.Bagheri, A.Afkhami, H.Khoshafar, M.Rezaei, A.Shirzadmehr; Simultaneous electrochemical determination of heavy metals using a triphenylphosphine/MWCNTs composite carbon ionic liquid electrode, Sensor Actuat B-Chem., **186**, 451 **(2013)**.

ORIGINAL ARTICLE

[51] S.Wang, Y.Wang, L.Zhou, J.Li, S.Wang, H.Liu; Fabrication of an effective electrochemical platform based on grapheme and AuNPs for high sensitive detection of trace Cu^{2+}, Electrochim.Acta, **132**, 7 **(2014)**.

[52] C.Gabrielli, O.Hass, H.Takenouti; Impedance analysis of electrodes modified with a reversible redox polymer film, J.Appl.Electrochem., **17(1)**, 82 **(1987)**.

[53] Jyh-Myng Zen, Yuan-Shih Ting; Square-wave voltammetric stripping analysis of lead(II) at a Nafion®/copper-mercury film electrode, Anal.Chim. Acta, **332(1)**, 59 **(1996)**.

[54] S.-Y.Shi, Z.-H.Fang, J.-R.Ni; Electrochemical impedance spectroscopy of marmatite-carbon-paste electrode in the presence and absence of *Acidithiobacillus ferroxidans*, Electrochem. Commun., **7(11)**, 1177 **(2005)**.

[55] F.Quentel; Voltammetric study of molybdenum in the presence of phenanthroline, Electroanal., **11(18)**, 1355 **(1999)**.

[56] Gary L.Long, J.D.Winefordner; Limit of detection. A closer look at the IUPAC definition, Anal.Chem., **55(7)**, 712A **(1983)**.