Carbon screen-printed electrodes modified by a polycatechol film for Cu and Pb detection in acidified drinking water

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CNRS / Univ Pau & Pays Adour / E2S UPPA, Institut des sciences analytiques pour l'environnement et les matériaux, UMR5254, 2 avenue Pierre Angot, 64000 Pau, France

**corresponding author: corinne.parat@univ-pau.fr*

Abstract

The dissolution of metals such as Cu or Pb in water can be increased by prolonged stagnation of water in internal pipes of drinking water networks, resulting in high concentrations in the consumer's tap water. As they can accumulate in biota and affect living organisms with more or less serious long-term toxic effects, the monitoring of Cu or Pb in tap water and more generally in aquatic environments is therefore an important issue. For this purpose, a new electrochemical sensor based on a screen-printed carbon electrode modified with a polycatechol film was developed for the highly sensitive detection of Cu and Pb in drinking water. The electropolymerisation was first optimised to obtain a homogeneous and reproducible film for the detection of trace metals. The mechanism of the polymerization process was proposed and discussed. Then, the performance of the new sensor was evaluated. The pH and the conductivity were found to be the main parameters influencing the sensitivity of the sensors. Thus, the electrochemical analyses carried out at pH values around neutrality with this device made it possible to determine the free and labile forms of metal in solution, while the total metal contents were determined after acidification of water samples to pH 5 or less. Furthermore, a stable signal was obtained from 470 µS cm^{-1}, which means that most of freshwater rivers and mineral waters can be directly analysed without any supporting electrolyte addition. After optimisation of the analytical conditions, a

sensitivity of the order of µg L^{-1} was reached for a deposition time of 60 s while an electrodeposition time of 300 s gave a sensitivity of ng L^{-1}.

Keywords: Electropolymerisation, *in situ* detection, trace metals, stripping chronopotentiometry

1. Introduction

The presence of metals such as lead (Pb) and copper (Cu) in water leaving water production facilities is low or undetectable. However, these substances can be found in higher concentrations in the consumer's tap water due to the dissolution of these metals in the water contained in the pipes (internal networks and possibly public connections), valves and fittings of the internal networks of buildings [1]. Concentrations in drinking water vary from 0.005 to 30 mg/L for Cu, mainly due to corrosion in internal Cu pipes, and are generally below 5 µg/L for Pb, although much higher concentrations (above 100 µg/L) have been measured in the presence of Pb pipes or fittings [2]. While there is still some uncertainty regarding the long-term effects of copper on sensitive populations [3], this is not the case of Pb which is recognized as a chemical of high public health concern. Thus, the quality limit in water intended for human consumption is currently set at 10 µg/L for Pb and at 2 mg/L for Cu by Directive 2020/2184 in accordance with the guide value recommended by the World Health Organisation (WHO) [4].

According to WHO, exposure must be assessed using an appropriate sampling strategy, taking into account when, where, and how samples are collected, as well as the number of samples to be collected [5]. Monitoring of metals in tap water and more generally in aquatic environments is therefore an important issue as they can accumulate in the biota and affect living organisms with more or less serious long-term toxic effects [6, 7]. Among the available analytical techniques, only a few approaches allow the implementation of suitable *in situ* devices in terms of analytical performance, autonomy, miniaturization feasibility, and ease of transport [8]. Due to their high sensitivity, electrochemical techniques, such as anodic stripping voltammetry (ASV) and stripping chronopotentiometry (SCP) using disposable sensors, have proven to be promising approaches for the analysis of metals in freshwater [9-14]. Among one single-

use sensors, screen-printed electrodes have been increasingly studied due to their performance and ability to be mass-produced at very low costs [15-18]. In addition, their surface can be easily modified, which has led to different improvements in the final sensor, such as increased selectivity and/or sensitivity. Most screen-printed sensors for sensitive determination of metals were based on a mercury film as a modifier of the working surface [19-21]. Due to the toxicity of mercury, several new types of mercury-free film electrodes have been developed for trace metal detection, such as bismuth-coated carbon electrodes [22-24] or gold-film electrodes [25-28]. Recent achievements show the electrochemical detection of trace metals with electrodes modified with inorganic, organic and biological materials [29-31]. Metal, metal oxide, carbon and silica-based nanomaterials have emerged as the most commonly used nanomaterials for electrochemical detection of trace metals [17, 32, 33]. Organic polymers have also been widely employed in sensor construction [34, 35]. Polyaniline, polypyrrole and poly(3,4-ethylenedioxytiophene) are the main conductive polymers used for biosensors due to their low-cost synthesis, high sensitivity, and excellent stability [36]. Catechol is a simple molecule, capable of establishing a wide range of interactions with organic and inorganic analytes [37, 38]. Depending on the pH, it also showed a tendency to form mono-, di-, or tri-coordinated complexes with metals like Cu, Zn, Ni, Co, Mn, Fe [39-42]. Thus, Koo *et al* demonstrated that a polycatechol film deposited on a glassy carbon electrode allowed the preconcentration of Ce(III) before its detection by differential pulse anodic stripping voltammetry [43].

All these works suggest that polycatechol is a good candidate for the development of an electrochemical sensor for *in situ* trace metal detection. The present study focused on the original development of an electrochemical sensor for Cu and Pb monitoring in drinking water. Our objective was to modify the working surface of a screen-printed electrode by a polycatechol film in order to form a time-stable, low-cost, robust and sensitive electrochemical platform for a direct metal detection in a freshwater sample. After optimizing the electrodeposition of the polycatechol film on a carbon-based screen-printed electrode (SPCE), the performance of the modified sensor for Cu and Pb detection was investigated and then tested in a mineral water sample.

2. Experimental

2.1 Chemicals and reagents

The polystyrene support for the screen printing was obtained from Sericol. The commercial ink (electrodag PF-407A) was purchased from Acheson Colloids. Acetic acid (CH_3COOH, Trace select), sodium acetate trihydrate (CH_3COONa, Trace select) were obtained from Fluka. Nitric acid (69-70%, Baker Instra-Analysed for trace metal analysis) and sodium hydroxide (Baker Analysed) were obtained from J.T. Baker. Mesitylen, disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot H_2O$), sodium phosphate monobasic (NaH_2PO_4) and 1,2-dihydroxybenzene (catechol) were purchased from Sigma-Aldrich. The stock solutions at 1000 mg L^{-1} of Cu and Pb were obtained from Merck. Ultrapure water (resistivity of 18 MΩ cm) was used for dilutions. Acetate buffer solution (0.1 mol L^{-1}, pH 4.6) was prepared by mixing appropriate amounts of CH_3COOH and CH_3COONa. Phosphate buffer (0.1 mol L^{-1}, pH 7.5) was prepared by mixing appropriate amounts of Na_2HPO_4 and NaH_2PO_4. Chemical composition of the mineral water was: calcium 68 mg L^{-1}, potassium 11 mg L^{-1}, magnesium 2 mg L^{-1}, sodium 21 mg L^{-1}, bicarbonates 219 mg L^{-1}, chlorides 28 mg L^{-1}, sulphates 39 mg L^{-1}, nitrates 1 mg L^{-1}, pH 7.6, conductivity 476 µS cm^{-1} (equivalent to 285 mg L^{-1}).

2.2 Instruments

All electrochemical measurements were performed on an Eco Chemie µAutolab III connected to a Metrohm 663 VA Stand and a computer using the GPES 4.9 software package (Eco Chemie). Electrochemical measurements were performed by means of a three electrode-system: a screen-printed carbon electrode (SPCE) with an active area of 9.6 mm^2 as working electrode, a carbon auxiliary electrode and an Ag/AgCl KCl (3 mol L^{-1}) reference electrode encased in a 0.1 mol L^{-1} KNO_3 jacket. A 3mm diameter glassy carbon electrode (GCE) from Syclope Electronique was also tested as a working electrode.

2.3 Preparation of catechol modified screen-printed electrode

The electrodes were manually screen printed on 1 mm-thick polystyrene plates using a commercial carbon-based ink to produce a set of 8 electrodes (Figure S1) [10]. After a drying step (1 hour at room temperature) and a curing step (1 hour in an oven at 60°C), an insulating layer (polystyrene dissolved in an adequate volume of mesitylene) was manually spread over the conductive track, leaving a working disk area of 9.6 mm^2 and an electrical contact.

The electrodeposition of catechol (1,2-Dihydroxybenzene) on the SPCE working surface was carried out in three steps. The following conditions correspond to the optimised conditions. The first step was the electrodeposition of catechol (10 mmol L^{-1}) on the working surface by cyclic voltammetry (CV) between -0.8 V and +0.8 V versus Ag/AgCl at scan rate of 200 mV s^{-1} in phosphate buffer (pH 7.2). The modified electrode was characterized by CV at 200 mV s^{-1}, using a monomer-free acetate buffer solution (pH 4.8). In a second step, the electrode was rinsed with water, immersed in 0.1 mol L^{-1} NaOH and cycled until a stable baseline was obtained. The final step was to air dry for 24 hours. The sensor is stored in the open air when not in use.

2.4 Electrochemical measurements

Trace metal measurements were performed at room temperature in a 0.1 mol L^{-1} acetate supporting electrolyte at pH 4.8 by SCP. Like the usual stripping voltammetry techniques, SCP requires two steps: a deposition (accumulation) step in which metal ions are reduced at a constant potential, followed by a stripping (quantification) step involving reoxidation by applying a constant oxidising current. The analytical signal is the time required for reoxidation (transition time τ). A reliable determination of τ is obtained by measuring the area under the peak in the dt/dE versus E plot, where dt/dE is the inverse of the time (t) derivative of the recorded potential (E) [44, 45]. After optimisation, the analytical parameters were as follows: an electrodeposition step of 60 s at -1.2 V with stirring, followed by an equilibration time of 10 s at -1.2 V without stirring and a stripping step by applying a stripping current (I_s) of 10 µA without stirring.

2.5 Analytical performance

Analytical performance (sensitivity, limit of detection and limit of quantification) of the modified SPCE was investigated using SCP, an analytical technique that allows the detection of trace metals at low concentrations (in the µg L^{-1} range) by applying the electrochemical parameters described above. Analyses were performed without purging at room temperature in a 0.1 mol L^{-1} acetate supporting electrolyte at pH 4.6, doped in Cu or Pb. Validation of the sensor was performed by SCP in a mineral water acidified at pH 4.6 with acetic acid, and doped in Cu at 40 µg L^{-1} in order to determine the total Cu concentration.

2.6 Statistical approach

The reliability of the sensor manufacture was based on the reproducibility, which was investigated by first comparing 8 modified SPEs from the same screen-printing plate (intra-plate reproducibility) and then by comparing 8 modified SPCEs from 8 different screen-printing plates (inter-plate reproducibility) (Figure S1). For each sensor, the mean Cu signal and its standard deviation, based on three replicates, were determined for a Cu concentration of 20 µg L^{-1} in a 0.1 mol L^{-1} acetate buffer.

The linearity and the sensitivity were obtained from the calibration plot based on 3 replicate analyses for each concentration. The linear regression analysis was performed by using the least squares method with the Excel analysis toolpak. This method was also used to calculate the slope and the intercept as well as their respective standard deviation.

The limit of detection (LOD) has been statistically determined from the calibration plot according to Eq. (1)

$$LOD = kS_b/m \qquad (1)$$

where k = 3, S_b is the intercept standard deviation of the regression line and m is the slope of the linear calibration plot [46]. The limit of quantification (LOQ) was calculated with the same equation as for the detection limit; however, the k-value was taken to be 10.

2.7 Speciation model

The geochemical modelling program *Visual Minteq*, ver. 3.0 (using the standard databases) [47] was used to predict metal speciation in mineral water. The following inputs were provided: pH, temperature (25°C), and total concentrations for Ca, Na, K, Mg, carbonates, nitrates, sulfates, chlorides, Cu and Pb.

3. Results and discussion

3.1 Electrochemical behaviour of catechol on SPCE

The functionalization of the transducer is an important step in the development of an electrochemical sensor, as it will determine the performance of the electrodes in terms

of sensitivity and stability over time. Our objective was first to optimise the electropolymerisation of catechol to obtain a stable and reproducible polycatechol film. Firstly, two types of electrodes were tested, SPCE and GCE. CV electropolymerisation of catechol showed that consecutive scans do not lead to a change in the anodic peak, suggesting that the polymer does not deposit on the GCE surface (Figure S2). Comparison of the electrode surfaces suggested that the rough surface of SPCE was more favourable for electropolymerisation than the smooth surface of GCE (Figure S3).

3.1.1 Effect of pH during electropolymerisation

As expected, CV performed in a solution of catechol at different pH values shows that redox processes are pH dependant (Figure 1). Whatever the pH, the first potential scan shows an anodic peak related to the oxidation of catechol to o-benzoquinone and a corresponding cathodic peak related to the reduction of o-benzoquinone to catechol. This redox process involves the transfer of two electrons and two protons [48, 49]. The following scans show a different behaviour depending on the pH. At acidic pH, the subsequent scans lead to a slight decrease of the anodic peak (5%) coupled with the appearance of a second oxidation peak at 0.21V, whose intensity increases with the cycles, suggesting the formation of a redox-active polymer film on the electrode surface [50]. This behaviour appears much more pronounced at neutral pH with the appearance of a second oxidation peak at 0.01V and a decrease in the catechol oxidation peak by 22% after 10 scans. The highest pH leads to a marked decrease in peak height (64%) with the appearance of a second oxidation peak at 0.72V suggesting a rapid dimerisation process in solution, leading to the depletion of catechol [48].

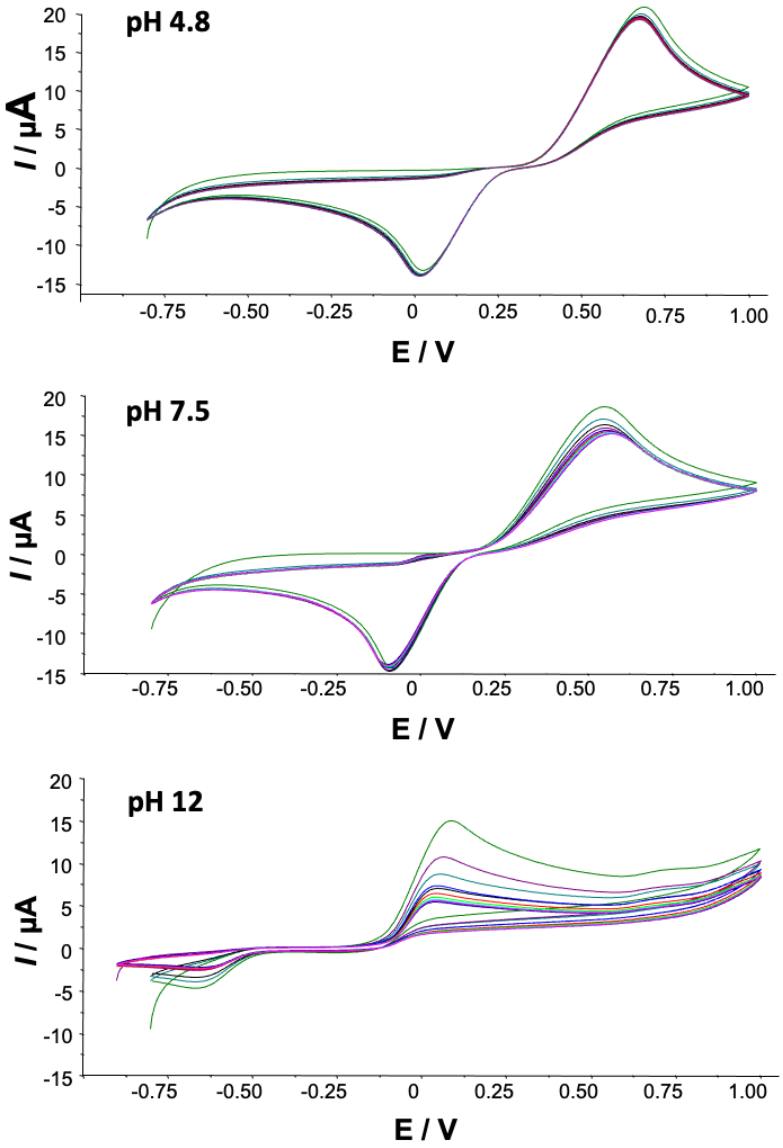

Figure 1. Electropolymerization of 0.5 mmol L^{-1} of catechol at different pH 4.8, 7.5 and 12.6. Cyclic voltammetry from -0.8 to 1V at 200 mV s^{-1}. First scan is represented in green and last scan in purple.

In order to check the deposition of the polycatechol film, CV were performed in acetate buffer solution without catechol. **Erreur ! Source du renvoi introuvable.** confirms that the polymerisation pH leads to different mechanisms of electrodeposition. An acidic pH allows the formation of a slightly electroactive film with only one redox couple. A basic pH does not lead to any significant modification of the electrode, compared to an unmodified electrode, which confirms the absence of polymerisation at this pH. On the contrary, neutral pH seems to be the most favourable for the formation of an electroactive polymer on the electrode surface with 3 redox couples observed in the blank solution, immediately after electropolymerisation [50]. These observations are in agreement with those of Marczewska (2013) who showed that the polymerisation process works from weakly acidic medium (pH 5.4) to weakly alkaline medium (pH

9.2) [51]. Moreover, it is interesting to note that air drying of the modified electrodes leads to a strong decrease in these redox peaks (not shown) suggesting an irreversible oxidation of the polymer by oxygen in the air. For this reason, the modified electrodes were then air-dried for 24 hours before use.

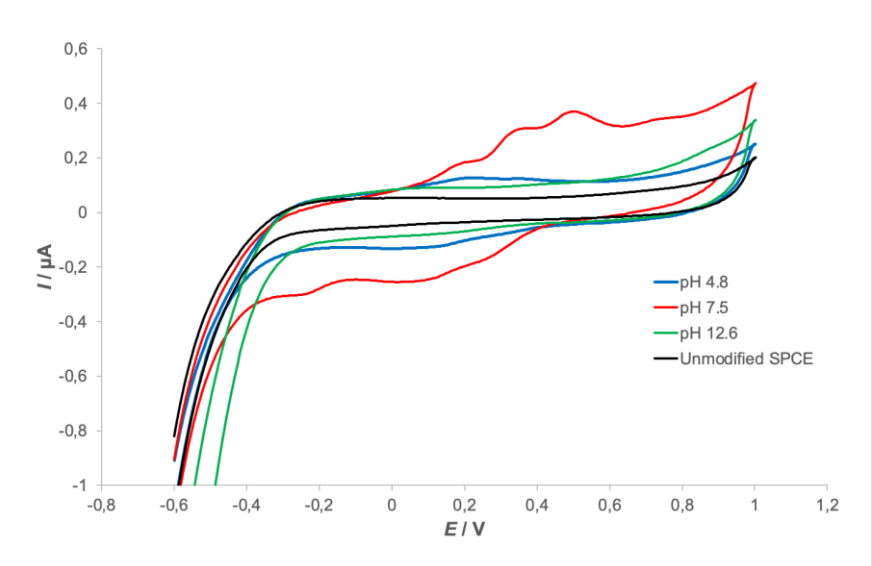

Figure 2. Cyclic voltammograms of polymerized SPCE at different pH in a blank solution (acetate buffer, 0.1 M, pH 4.8). Scan rate: 200 mV s^{-1}.

The proposed mechanism to explain the formation of an electroactive film on the electrode is the formation of a polymer *via* the coupling of mesomeric structures of phenoxy radical [52, 53]. Ortho-semiquinones, formed during the reduction steps from orthoquinones, are highly reactive species capable of reacting to form higher oligomers resulting in film deposition. When two of these ortho-semiquinones are sufficiently close, they undergo aryl-aryl coupling and progressive film deposition by polymerisation [54].

We can therefore conclude that the polymerisation process is initiated by the production of free radicals following the electrochemical oxidation of catechol to benzoquinone and its subsequent reduction to ortho-semiquinone (Figure S4). Once this radical initiator is formed, it attacks another monomer to initiate a polymer chain. Redox cycles allow the chain to propagate. Termination occurs during air drying, with oxygen acting as a polymerisation inhibitor.

The acidity dissociation constants (p*K*a) for its hydroxyl groups are both above 7: pKa_1 = 8.83 and pKa_2 =13.07 [55]. Changing the pH of the catechol solution leads to a change in and the dissociated forms and their concentration. Thus, at pH 7.5, the

monoanion starts to form (between 2 and 4% depending on the p*K*a value) whereas at pH 12, the catechol is in anionic form only. At higher pH, Pourghobadi *et al* proposes an alternative mechanism based on anionic or dianionic forms of catechol as nucleophiles that would rapidly add to the electrochemically generated o-benzoquinone, the rate of the dimerisation reaction increasing with pH [56].

As our objective was to optimize and control the deposition of the film catechol on the surface of the working electrode, a pH of 7.5 was chosen for catechol electropolymerisation.

3.1.2 Effect of scan rate during electropolymerisation

Figure 3A shows the first and 10th scan obtained during electropolymerisation with different scan rates from 20 (red line) to 200 mV s^{-1} (black line) in a phosphate buffer solution (0.1 M, pH 7.5) containing 0.5 mmol L^{-1} of catechol. Increasing the scan rate induces an increase in peak height (x2.5), and in ΔE_p (from 0.38 to 0.61V). The effect of scan rate on the properties of the polymer film was then studied in an acetate buffer solution at pH 4.6 (Figure 3B). Regardless of the scan rate, the polymerization of catechol leads to a film with 3 redox reactions (3 redox peaks). The lowest scan rate results in the highest capacitive current, while the other 3 scan rates give exactly the same voltammogram (Figure 3B). The slower the potential scan rate, the longer the life time of the semi-quinone radicals and the higher the probability of depositing thicker films with larger oligomers [54]. On the contrary, a high scan rate (200 mV s^{-1}) allows linear polymer growth due to a conductive and/or porous polymer matrix [57]. Therefore, a scan rate of 200 mV s^{-1} was chosen for the next experiments.

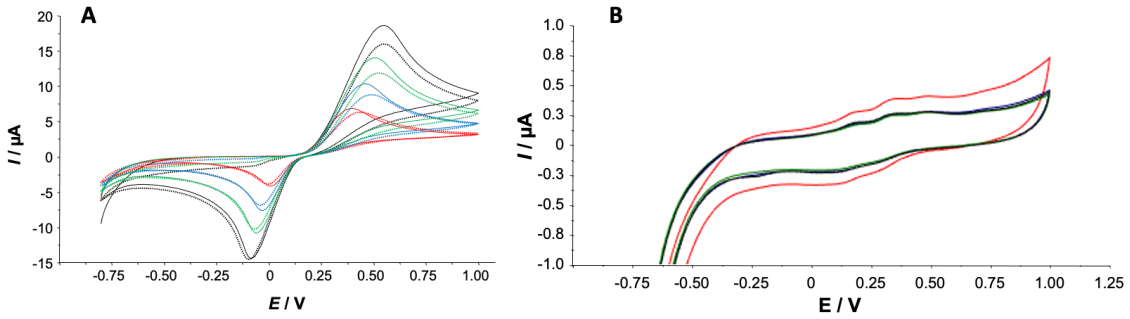

Figure 3. CV of polymerized SPCE at different scan rates: red line: 20 mV s^{-1}, blue line: 50 mV s^{-1}, green line: 100 mV s^{-1} and black line: 200 mV s^{-1} in a 0.5 mmol L^{-1} catechol solution (pH 7.5). **A** - first scan (solid line) and last scan (dotted line) of catechol film polymerization; **B** – CV in a 0.1 M acetate buffer solution (pH 4.8; scan rate: 200 mV s^{-1}).

3.1.3 Effect of scan number during electropolymerisation

Figure 4 shows the effect of the number of scans on the properties of the polymer film. The polymer films obtained after 10, 20 or 50 scans show similar behaviour. Voltammograms obtained in acetate buffer solution show that the capacitive current does not increase with the number of polymerisation cycles suggesting that the polymer is porous and/or conductive (Figure 4). According to Almeida et *al.*, the mass growth profile of polycatechol is approximately linear during the 50 polymerization cycles due to the continuous oxidation of catechol at the electrode surface [38]. Consequently, an electropolymerisation of catechol based on 50 CV was retained for the following experiments which aim to detect trace metals in freshwater samples.

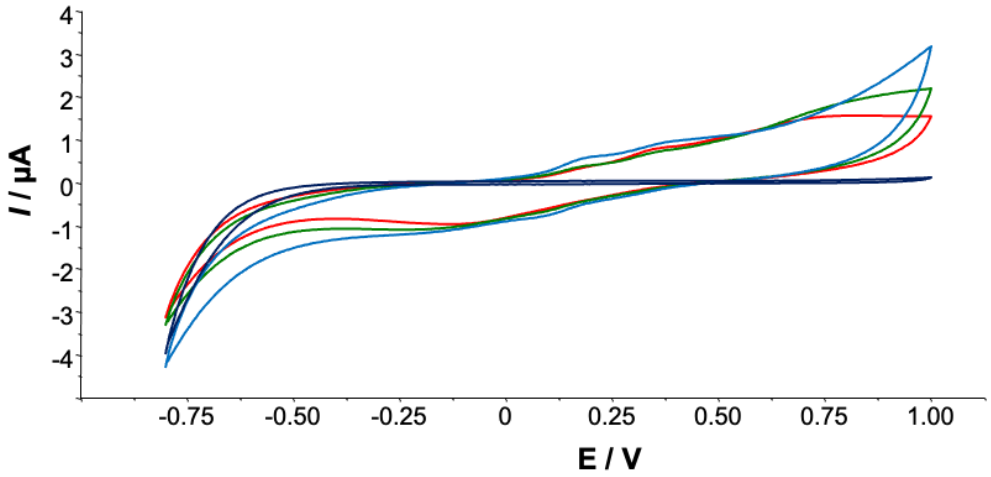

Figure 4. CV of polymerized SPCE from different scan number (black line: unmodified SPCE, red line: 10 scans, green line: 20 scans and blue line: 50 scans) in a blank solution (acetate buffer 0.1 M at pH 4.8; scan rate: 200 mV s^{-1}).

3.2 Electrochemical detection of Cu and Pb by stripping chronopotentiometry

3.2.1 Optimization of the stripping current

By varying the applied stripping current, the stripping time regime can be varied from semi-infinite linear diffusion conditions ($I\tau^{1/2}$ constant) to conditions approaching complete depletion ($I\tau$ constant) [44]. These fully depletion conditions are particularly attractive for *in situ* application in samples such as freshwater as they lead to greater sensitivity, and are not affected by adsorption effects [58]. They allow measurements to be made without removing oxygen from the solution [11]. These conditions are therefore suitable for *in situ* analyses of Cu and Pb. The influence of the stripping

current on the Cu signal was evaluated in order to establish the experimental conditions under which the complete depletion regime was reached. Figure S5 shows that for the values of I_s between 1 and 20 µA, the complete depletion regime $I\tau$ (constant) is reached from stripping currents between 5 and 20 µA. Regardless of the value of I_s, plotting $I\tau^{1/2}$ as a function of I_s never resulted in a plateau. As a result, a stripping current of 10 µA was chosen for the following experiments.

3.2.2 Analytical performance of the modified SPCE for metals determination

The calibration plot for Cu in a sodium acetate solution buffered to pH 4.6 shows that a sensitivity of 0.0044 ± 0.0005 s/µg L^{-1} and a linearity of 5 µg L^{-1} to 100 µg L^{-1} can be obtained, which corresponds to working conditions well suited to the detection of Cu in drinking water (Figure 5A and 6B). A LOD of 2 µg L^{-1} and a LOQ of 7 µg L^{-1} were obtained for a preconcentration time of 60 s. Similar results were obtained for Pb with a LOD of 2 µg L^{-1} and a LOQ of 6 µg L^{-1}, although this sensor appeared less sensitive for Pb with a slope of 0.00075 ± 0.00002 s/µg L^{-1} (Figure 5C and 6D). These results are promising for monitoring purposes as a measurement time of 60 s allows the detection of concentrations in the µg/L range which is in perfect agreement with the values set by legislation.

However, these values could be improved by increasing the deposition time since the longer the deposition time, the higher the amount of analyte is available at the electrode during the analysis (Figure S6). Thus, for Pb, increasing the electrodeposition time from 60s to 300 s resulted in a calibration line between 100 and 500 ng L^{-1} with a LOD of 63 ng L^{-1} and a LOQ of 92 ng L^{-1} (Figure S7). These results are slightly higher than those of Poudel et al for Pb who obtained a LOD of 3.7 ng/L after a waiting time (extraction and reduction) of 1060 s which does not allow continuous *in situ* monitoring [59]. Higher concentrations can also be detected by using an electrochemical method less sensitive such as linear scan voltammetry which allows the detection of Cu up to 5 mg L^{-1} (Figure S8). These results show the power of the electrochemistry to detect a wide range of concentrations from ng L^{-1} to mg L^{-1}, only by modifying the electrodeposition time and/or the electrochemical method.

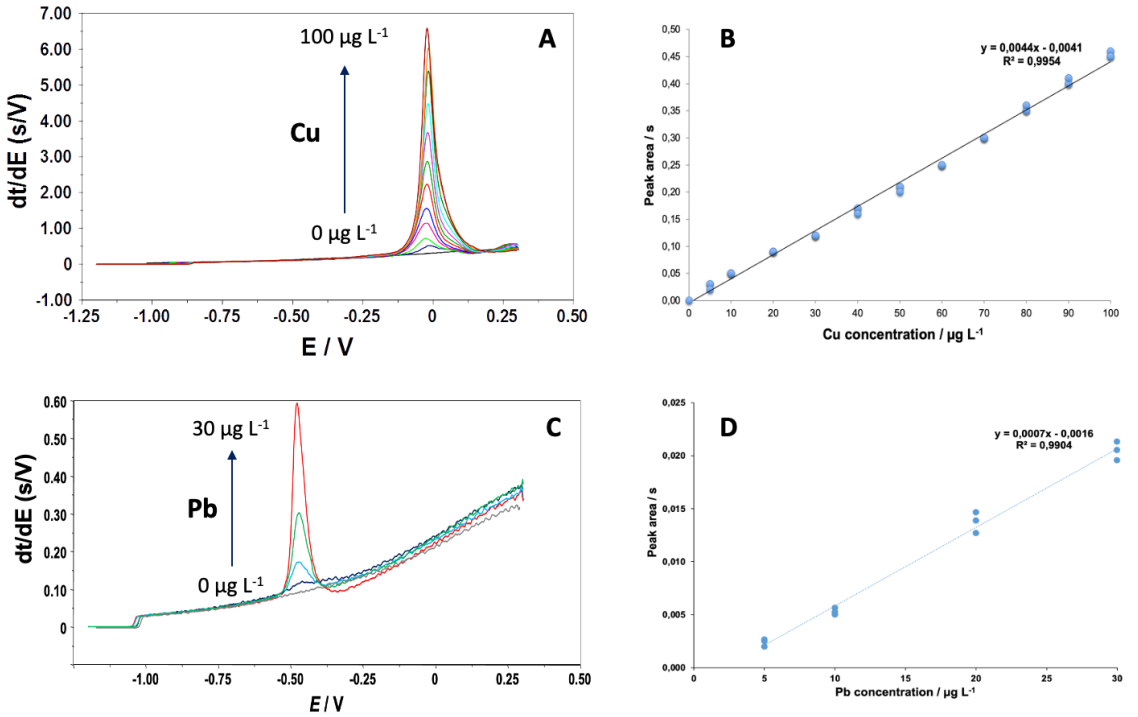

Figure 5. Stripping Chronopotentiometric response of Cu (**A**) and Pb (**B**) and calibration plot of Cu (**C**) and Pb (**D**) obtained with a modified SPCE in acetate buffer 0.1 mol L^{-1}. Analysis conditions: electrodeposition: 60 s at -1.2 V with stirring, equilibration time 10 s at -1.2 V without stirring, stripping current I_s =10 µA without stirring.

3.2.3 Repeatability and reproducibility

Figure S9 shows Cu signal obtained for 8 modified SPCEs coming from the same screen-printing plate (Figure S9A) and for 8 modified SPCEs from 8 different screen-printing plates (Figure S9B). No significant difference was observed between the different modified electrodes, where a Cu concentration of 20 µg L^{-1} led to a peak area of 0.064 s ± 0.004 s for electrodes from the same plate and of 0.072 s ± 0.005 s for electrodes from different plates. This result underlines the robustness of the sensor construction, from serigraphy to modification of the surface, which is promising for the development of a field sensor.

3.2.4 Simultaneous detection of Cu and Pb

Figure 6A shows the Pb signal obtained that simultaneous detection of Pb and Cu is not a problem as these metals don't have the same redox potential with -0.48 V for Pb and +0.06 V for Cu. The addition of Cu in the solution doesn't change the Pb signal which suggests that there is no interference. However, Figure 6B shows that the calibration plot obtained for Cu concentrations from 1 to 4 µg L^{-1}, in the presence of 30 µg L^{-1} of

Pb gives a slope of 0.0034 ± 0.0002 s/µg L^{-1} which is slightly lower than that obtained in the absence of Pb (0.0044 ± 0.0005 s/µg L^{-1}). On the contrary, when the Cu/Pb concentration ratios are reversed, the Cu signal is little affected by the presence of Pb (Figure S10). All these results mean that in the case of a multi-metal contamination, a calibration taking into account the different metals in solution will be necessary to obtain an accurate value.

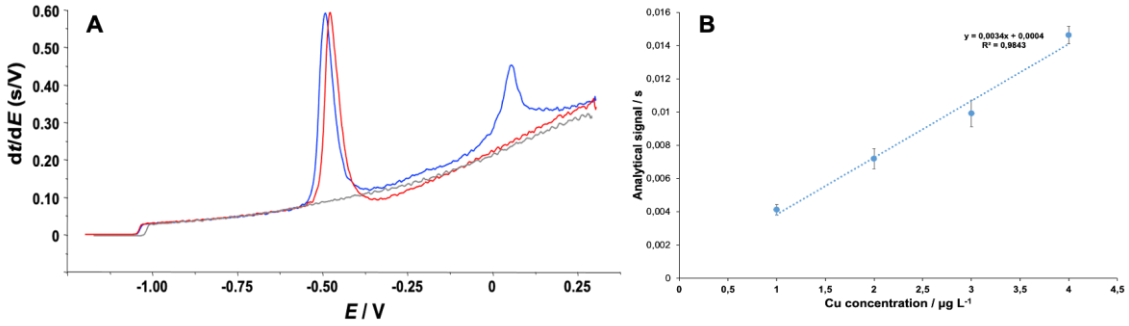

Figure 6. A - Analytical signal of Pb (30 µg L^{-1}) without or with Cu (4 µg L^{-1}); **B** - Calibration plot of Cu from 1 to 4 µg L^{-1} in presence of Pb at 30 µg L^{-1}. Analysis conditions: acetate buffer 0.1 mol L^{-1} at pH 4.6, deposition at -1.2 V for 60 s, stripping current I_s = 10 µA.

3.2.5 Effect of the conductivity of the sample

Conductivity is also an important parameter to take into account when analysing natural freshwater samples because this parameter can strongly change from one sample to another. Parat *et al* analysed different natural freshwaters from some rivers in the Pyrenees (France) and found conductivities ranging from 78 to 211 µS cm^{-1} [13] while Platikanov *et al* who collected tap waters from different locations in Catalonia (Spain), found conductivities ranging from 82.3 µS cm^{-1} to 2417 µS cm^{-1} [60]. Therefore, the effects of solution conductivity on Cu signal were studied in ultrapure water doped with Cu at 50 µg L^{-1} in which successive additions of acetate (1 mol L^{-1}) were made. Figure 7 shows the variation of the signal (peak area) obtained for Cu at different conductivities, with a plateau from a conductivity of 470 µS cm^{-1}, a value close to those found in most natural freshwaters.

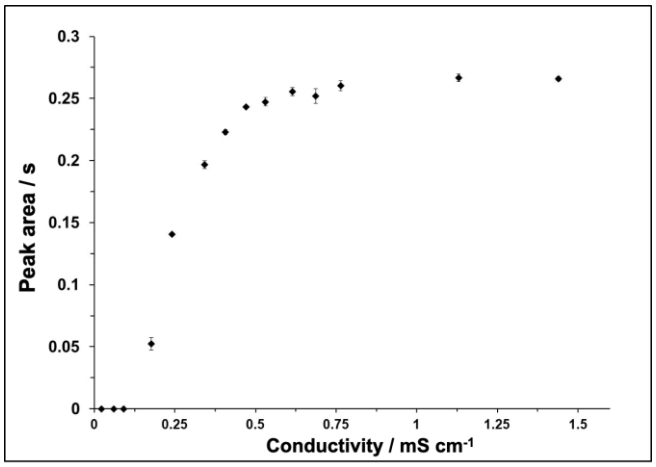

Figure 7. Effect of conductivity on Cu signal (Cu concentration = 50 µg L^{-1}) obtained with a modified SPCE. Analysis conditions: electrodeposition: 60 s at -1.2 V with stirring, equilibration time 10 s at -1.2 V without stirring, stripping current I_s = 10 µA without stirring.

3.2.6 Effect of pH on water samples

The effect of pH on the response of the modified SPCE in the presence of Cu was studied over a pH range of 3 to 7.6. The pH was adjusted to the different values by adding acetic acid to mineral water. The signal shows a stable peak area between pH 3 and 5 (Figure 8). At higher pH, a sharp decrease in signal is observed from 57% at pH 6 to 82% at pH 7.6. This behaviour can be due to the inorganic compounds (bicarbonates, sulphates and nitrates) present in the solution, and capable of forming Cu complexes, which are not electrolabile. The Visual MINTEQ speciation model confirms that the proportion of free Cu in mineral water depends on pH with only 3.8 % of free Cu at pH 7.6. At this pH, carbonates appear as the main compound complexing Cu (90%) and blocking its electrochemical detection (Table 1). Acidification of the sample with acetic acid from pH 7.6 to 4 changes the Cu speciation leading to 69 % of free Cu and about 27% of Cu-acetate complexes that are electrolabile. Lead shows the same behaviour with about 88% of Pb-carbonate complexes at pH 7.6 and only 5.6 % of free Pb. The acidification of the solution leads to a modification of the speciation with about 95% of labile Pb (Table S1). This means that the determination of the total concentration of Cu and Pb will require a prior acidification of the solution at pH 5 or less to dissociate Cu and Pb carbonate complexes present in solution.

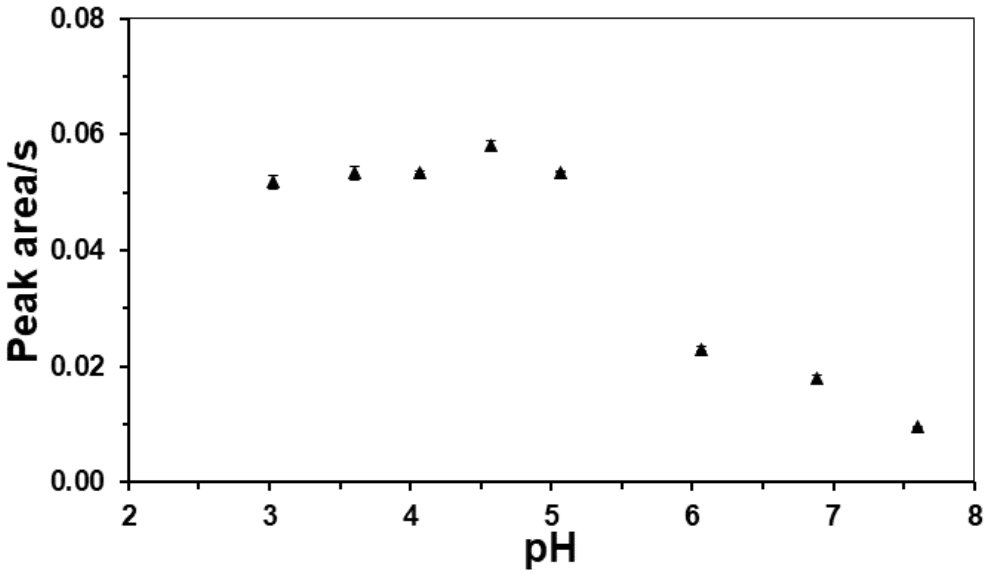

Figure 8. Variation of Cu signal according to the pH obtained with a catechol modified SPCE in a mineral water. Analysis conditions: Cu concentration: 20 µg L^{-1}, electrodeposition: 60 s at -1.2 V with stirring, equilibration time 10 s at -1.2 V without stirring, stripping current I_s =10 µA without stirring.

Table 1. Speciation of Cu (in %) computed from Visual Minteq 3.0 in mineral water at pH 7.6 and acidified with acetic acid from pH 7 to 4

	pH 7.6	pH 7	pH 6	pH 5	pH 4.6	pH 4
Cu^{2+}	3.8	14.9	62.7	69.4	69.1	68.9
$CuOH^{+}$	3.7	3.6	1.5	0.2	0.1	
$Cu(OH)_2$ (aq)	0.2	0.1				
$CuCl^{+}$			0.1	0.1	0.1	0.1
$CuSO_4$ (aq)	0.1	0.6	2.3	2.6	2.6	2.5
$CuCO_3$ (aq)	89.6	77.7	13.1	0.2		
$CuHCO_3^{+}$	0.6	1.9	3.3	0.5	0.2	0.1
Cu-Acetate^{+}	2.0	0.4	16.5	25.9	26.7	27.2
Cu-$(Acetate)_2$ (aq)		0.8	0.5	1.1	1.2	1.2

3.3 Analysis of acidified mineral water by using modified SPCE

A calibration plot was carried out in a mineral water sample previously acidified with acetic acid to dissociate all Cu-complexes (Figure 9) and compared to that obtained in acetate solution. The deposition time and SCP parameters were the same as those used previously. A slope of 0.0041 s/µg L^{-1} was obtained in acidified mineral water which is similar to that obtained in 0.1 mol L^{-1} acetate buffer (0.0044 ± 0.0005 s/µg L^{-1}) showing that no interfering effect occurs in a solution such as a mineral water.

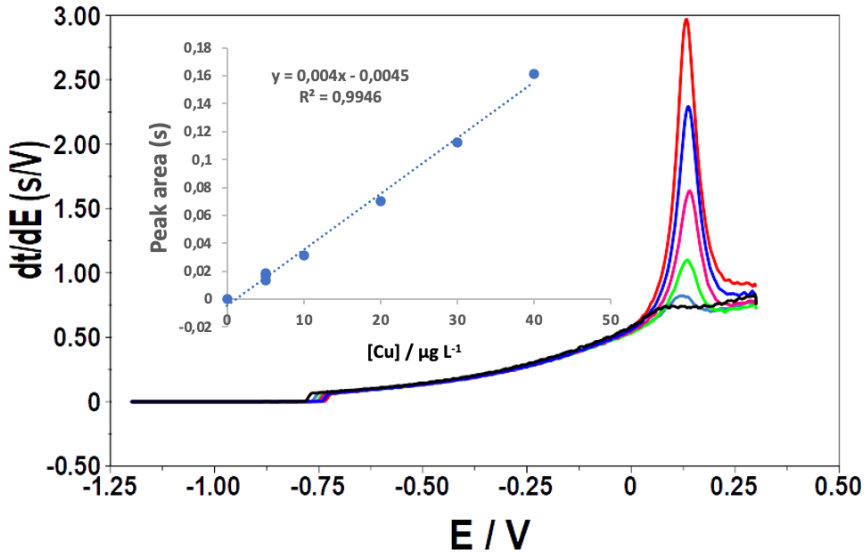

Figure 9. Stripping chronopotentiometric response and Cu calibration plot obtained with modified SPE sensor in the presence of different copper concentrations in acidified mineral water (pH 4). Analysis conditions: electrodeposition: 60 s at -1.2 V with stirring, equilibration time 10 s at -1.2 V without stirring, stripping current I_s = 10 µA without stirring.

4. Conclusion

A new electrochemical sensor has been developed for the detection of Cu and Pb in acidified drinking water. For this purpose, a screen-printed carbon electrode was modified by a polycatechol film. Different parameters were studied to obtain a homogeneous and stable film, as the effect of pH, the scan rate and the number of electropolymerisation scans. Optimisation of the polymerisation conditions resulted in a highly reproducible electrochemical platform indicating a simple and robust method of sensor fabrication.

High performance was achieved using stripping chronopotentiometry (SCP) to detect Cu and Pb in acetate buffer at pH 4.6. We showed the power of the electrochemistry to detect a wide range of concentrations from ng L^{-1} to mg L^{-1} with the same working electrode, only by modifying the electrodeposition time and/or the electrochemical method (SCP or LSV).

From a more general point of view, compared to previous studies aimed at developing electrochemical sensors for trace metal detection in drinking water, we demonstrate for the first time an efficient and sensitive electrode based on a polycatechol film. This preparation method is interesting because it can easily replace the deposition of expensive, toxic (mercury film) and sometimes complicated synthetic molecules like cyclodextrins and calixarene used for detection of trace metal such as Cu. The analytical performances obtained, namely a good reproducibility, a good repeatability and a

sensitivity range in agreement with the concentrations found in acidified mineral water for Pb and Cu for measurement time between 60 s and 300s, make this modified SPCE an ideal candidate for industrialisation for monitoring the aquatic environment.

Research is underway to develop an industrial sensor where the three electrodes (working, auxiliary and reference) would be combined on a single sensor.

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