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Ignacio Pedre, Lucila Paula Méndez De Leo & Graciela Alicia González

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RESEARCH PAPER

Cu²⁺ ion-sensitive surface on graphite electrodes

Ignacio Pedre¹ · Lucila Paula Méndez De Leo¹ · Graciela Alicia González¹

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Abstract



A new electrochemical interface based on polyacrylic acid (PAAcid) immobilized in a Nafion® polymeric matrix on graphite screen-printed electrodes for detecting copper is presented. The copper is retained in the surface due to the capacity of the polyacid to chelate metals, and quantified using square wave voltammetry. The response was characterized by spectroscopic techniques (UV-vis-IR), which confirmed the chelation from the Cu^{2+} ions by the acid. A calibration curve is presented, showing good linearity and repeatability and its usefulness as a sensor. The range of operation goes from 15 to 50 μ M, with a detection limit of 12 μ M, making the sensor useful for measurements in environmental samples (after a preconcentration step) and in drinking water.

Keywords Copper · Sensitive interface · Environmental electroanalysis · FT-IR characterization

Introduction

Heavy metals represent a serious threat for natural water systems, because they are persistent and can be accumulated in living organisms, and therefore biomagnified in the upper levels of the food web. For these reasons, increased attention is paid to their detection and removal from contaminated water and wastewater, and their permissible upper limits in water and food decrease each year [1]. Metals and metalloids such as Cu, Cd, Al, Cr, Zn, Fe, Hg, As, and Pb are often released in large quantities during or after the mining activity and can lead to the pollution of aquatic ecosystems.

Conventional analytical methods for the determination of metals at low concentrations include the use of techniques such as atomic spectroscopies (atomic absorption spectroscopy, induced coupled plasma), ultraviolet-visible spectroscopy, ion chromatography, capillary electrophoresis, and X-ray fluorescence spectroscopy. Although these analytical methods show excellent figures of merit in terms of selectivity and sensitivity, their major disadvantages are the tedious sample preparation and the use of expensive instrumentation. On the other hand, these determinations cannot be performed on the field. Therefore, an accurate, fast, miniaturized, inexpensive, and sensitive means of monitoring metals in environmental samples and drinking water is highly desirable [2]. The method should be simple so that it can be easily operated by a layman.

In particular, copper is an important element for the industry (electroplating, printed circuits, fertilizers, etc. [3]), and although it is essential for the living organisms and the environment, it becomes dangerous when present in high concentrations [2]. For example, in humans, an excessive ingestion of Cu^{2+} may cause serious health problems such as Wilson, Menkes, and Alzheimer's diseases, and for that reason, its permissible concentration level in drinking water has been regulated by the US EPA as 1.3 mg/L (20 μ M) [4]. Copper is also considered a water pollutant, which can reach water bodies through natural processes and anthropogenic activities such as mining and petroleum refining [5].

Although copper concentrations in environmental samples vary greatly depending on the source, the location, and the sampling method, we include some values as a guide: as mentioned before, the permissible limit in drinking water is 20 μ M. On the other hand, according to [6], concentrations of copper in natural waters range from 17 to 24 nM in rivers, 5 to 20 nM in lakes, 0.5 to 5 nM in the Pacific Ocean, and from 10 to 300 nM in rain water. Other sources [7] estimated a world average concentration of copper in rivers to be

[☑] Ignacio Pedre ipedre@qi.fcen.uba.ar

Graciela Alicia González graciela@qi.fcen.uba.ar

¹ INQUIMAE – Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, Pabellón 2, 1428 Buenos Aires, Argentina

23.6 nM Cu dissolved load and 100 mg/kg Cu suspended particulate load. The high Cu content in suspended material is due to the presence of surface functional groups, for example, in humic substances, that are able to coordinate metallic cations [6].

Some quantification methods for Cu²⁺ using fluorescent probes, with varying degrees of sensitivity, selectivity, applicability, and difficulty of preparation, have been reported [8]. One example is the method reported in [3], where dipsticks for Cu²⁺ detection in drinking water were developed based on the quenching of sulforhodamine 101 fluorescence in the presence of a Cu-cuprizone complex. The employed techniques were fluorescence spectroscopy and red-green-blue (RGB) readout of digital imaging. The limit of detection for these sensors was 2 nM; the method is hardly affected in a pH range from 4.0-7.0 and only 5 min of incubation time was required. The selectivity for Cu(II) is high, even in the presence of various heavy metals. Another fluorescence chemosensor was reported in [4]. It is based on the aggregation-induced emission characteristic of bis(pyridin-2-ylmethylene)terephthalohydrazide. The sensor shows highly sensitive and selective response to Cu²⁺ over other metal ions. Cu²⁺-induced fluorescence quenching was proportional to the concentration of the analyte, being the low limit of detection 160 nM. One disadvantage of these two sensors is the requirement of rather specific dyes. Santos et al. [9] reported a sequential injection-lab on valve method that makes use of solid-phase spectrophotometry for the detection of Cd, Zn, and Cu in freshwaters. The limit of detection for this method is 2 nM.

An example of electrochemical sensors is the one reported in [10], which is a potentiometric sensor consisting of a polymeric film modified with graphite ink containing 2-N,Ndimethylcarbamimidoyl (metformin) as Cu-complexing agent. The electrodes are applicable to water samples and biological fluids from Wilson's patients. The limit of detection for Cu^{2+} is 1 μ M, and the selectivity of the sensor for copper is good. Other electrochemical sensors have been developed for the detection of Cu^{2+} in seawater, as shown in [5]. For example, Herzog et al. [11] fabricated electrochemical (impedimetric and voltammetric) sensors based on microelectrode arrays for the detection of copper. The sensors are fabricated on silicon using photolithographic and thin film deposition techniques. The impedimetric sensor is made of Pt electrodes used for the measurement of conductivity. On the other hand, the voltammetric sensors consist of a three-electrode electrochemical cell with a working on-chip platinum counter and Ag/AgCl reference electrodes, which are used to detect copper by underpotential deposition-stripping voltammetry at microelectrode array. The Cu²⁺ concentration range in which the sensors were useful was 0.48 to 3.97 µM. However, the photolithographic and thin film deposition techniques do not make the sensors simple to construct. On the other hand, the use of Pt electrodes makes them more expensive.

The advantages of electrochemical sensors are their simplicity, rapidity, sensitivity, and selectivity, apart from the fact that the required equipment is economically accessible, and the protocols can be adapted for use by personnel after a short training. Therefore, we developed a simple way to modify a conductive surface of graphite to build a sensitive interface to monitor Cu^{2+} ion in effluents and drinking and natural water samples.

Nafion® is a sulfonated tetrafluoroethylene-based copolymer highly stable against chemical attacks, being its main use as a proton-conducting ionomer in fuel cells. Polyacrylic acid (PAAcid) is the homopolymer of acrylic acid, and is stable in strong acids and bases [12]. This polymer, being a weak anionic polyelectrolyte at pH higher than 5–6, can associate with various non-ionic polymers (such as polyethylene oxide, polyacrylamide, etc.) via hydrogen-bonded inter-polymer complexes or with oppositely charged polymers, like chitosan, to form poly-complexes.

The use of Nafion® in metal-sensing devices was reported in [13]. The method described uses glassy carbon electrodes coated with the polymer. Bismuth and the analyte are electrodeposited jointly and copper is detected by stripping voltammetry. However, the method is applied using a rotating disk electrode, which makes it unsuitable for field measurements. The electrode was applied to different real samples such as tap water, urine, and wine. The article makes use of the anodic stripping voltammetry technique. The achieved limits of detection were 0.1 μ g/L for Cd and Pb and 0.4 μ g/L for Zn, and the linear ranges were 1 to 20 μ g/L for all three metals.

Particularly relevant is the reported article using Nafion®modified graphite screen-printed electrodes for the determination of Fe³⁺ in drinking water [14]. The employed technique was square wave voltammetry. Prior to measurement, an electrodeless preconcentration was applied. Nafion is a chemically inert polymer and endows remarkable sensitivity for Fe(III) through interaction with the sulfonic groups on the polymer surface. The linear range starts at 50 nM and ends at 5.00 μ M.

In this work, we present a novel polymeric matrix for the development of electrochemical platform suitable to determine copper in fresh-, drinking-, and seawater. The polymeric matrix was resistant to these high salinity conditions, making the sensor suitable for measuring in seawater samples. The use of exchange resins is customary to bring the concentrations of metal ions from seawater samples to measurable concentrations even by conventional techniques. The PAAcid is easily dissolved in the matrix and the resulting mixture can be applied to graphite screen-printed electrodes by drop casting, thus giving a simple modification procedure. Therefore, this modification process can be considered as a convenient alternative to other modification methods such as covalent linkage [15, 16], layer by layer polyelectrolyte assembling [17, 18], or polymer brushes [19], and its use can easily be extended to

Materials and methods

Chemicals and reagents

Sodium chloride (Carlo Erba, CAS 7647-14-5), Nafion® 5 wt% solution in a mixture of water and lower aliphatic alcohols (Sigma Aldrich, CAS 31175-20-9), polyacrylic acid with average $M_w = 1800$ (PAAcid, Sigma Aldrich, CAS 9003-01-4), and copper sulfate (Mallinckrodt, CAS 7758-98-7) were analytical grade reagents, and were used without further purification. All solutions were prepared with deionized water (resistivity > 18 M Ω cm) obtained from a Millipore® system. The pH of 3.5% NaCl solutions was 6.56. After addition of 100 μ M CuSO₄, the pH dropped to 6.25.

Construction of the electrodes

The system consisted of graphite screen-printed electrodes (Fig. 1) made in a way similar to the ones reported in [20] and modified as indicated below. The electrodes were provided by Donflex Saja S.R.L. (Buenos Aires, Argentina) with the working, counter, and reference electrodes integrated in one array designed to be connected to a USB female connector. The working electrode had an area of 0.64 cm² and the counter electrode 1.13 cm². The reference electrode was a silver surface which was treated with sodium hypochlorite in basic medium (55 g L⁻¹ active chlorine) for 5 min and then rinsed with water, resulting in suitable pseudo reference electrodes. The potentials in this work are expressed vs. Ag/AgCl.

Working electrodes were modified with 8 μ L of Nafion® solution or a mixture of 100 μ L Nafion® solution and 10 μ L of PAAcid in water (30 mg/mL). The sensors were left to dry at room temperature and used the following day. This



Fig. 1 Screen-printed electrodes used for sensing metals in environmental samples

modification resulted in robust and stable electrodes, which showed the same standard deviation as the values reported for the calibration curve for at least 1 week after preparation.

Electrochemical measurements

Square wave voltammograms (SWV) were measured with a μ AUTOLAB type III potentiostat run on a PC using GPES® (General Purpose Electrochemical System) software. Voltammograms were measured in the presence of 3.5% NaCl solution containing varying concentrations of Cu²⁺ ion (as CuSO₄); after applying to the electrodes, the treatments are detailed in Table 1.

Spectrophotometric measurements

Visible absorption spectra were measured using a modular Ocean Optics DT-Mini-2 spectrophotometer with a diode array detector and a 1-cm light path quartz cell connected to a PC and operated through SpectraSuite software. The measured solutions were 50 mM CuSO₄ and 50 mM CuSO₄ + 15 mg/mL PAAcid. The pH was adjusted to 2 with H_2SO_4 .

Infrared measurements

Infrared spectra were measured in transmission mode with an IR Thermo Nicolet 8700 instrument with DTGC detector (deuterated triglycine sulfate detector) operated by Omnic® software. A silver chloride window was modified with 8 μ L of Nafion® or Nafion® + PAAcid and left to dry on air. The window was successively modified with Nafion® + PAAcid mixture at its natural pH (3), and at pH values 6 and 13, being the pH adjusted by adding negligible volumes of concentrated NaOH. Typically, 32 spectra with a resolution of 4 cm⁻¹ were averaged. IR spectra were measured for these windows before and after incubating 5 min with 3.5% NaCl or 3.5% NaCl and 0.1 M CuSO₄, reproducing the electrode treatment. After the incubations, the windows were rinsed twice with drops of water and dried gently with paper towel.

Results and discussion

Square wave voltammetry measurements

Figure 2 shows the voltammograms corresponding to the concentrations 0, 100, 250, and 500 μ M Cu²⁺ measured using the A–D treatments (Table 1). In Fig. 2, the column from the left refers to electrodes without PAAcid (only Nafion®), and the one on the right to sensors containing the polymer. As mentioned above, the conditions for the square wave voltammograms were frequency = 8 Hz, step potential = 5 mV, and amplitude = 20 mV.

Table 1 Incubation and SWV conditions employed								
Treatment	Incubation time	Incubation solution	Measurement solution	SWV conditions				
A B	None 5 min	None Cu ²⁺ 0–500 μM + NaCl 3.5%	Cu ²⁺ 0–500 μM + NaCl 3.5% Cu ²⁺ 0–500 μM + NaCl 3.5%	0.3 to -0.1 V vs. Ag/AgCl Frequency = 8 Hz Step potential = 5 mV Amplitude = 20 mV				
C D	5 min 5 min	Cu ²⁺ 0–500 μM + NaCl 3.5% NaCl 3.5%	NaCl 3.5% Cu ²⁺ 0–500 μM + NaCl 3.5%					

From these graphs, the following observations can be withdrawn. In the first place, a reduction current can be observed in the presence of copper ion at around 50 to 150 mV vs. Ag/ AgCl. When PAAcid is added to the polymeric matrix, no

Fig. 2 Square wave voltammograms corresponding to the concentrations 0, 100, 250, and 500 $\mu M~Cu^{2+}$ in 3.5% NaCl under various conditions. Frequency = 8 Hz, step potential = 5 mV, amplitude = 20 mV. The potential was swept from positive to negative potentials. a to d Electrodes modified with Nafion®, treatments A to D respectively (Table 1). e to h Electrodes modified with Nafion® and PAAcid, treatments A to D respectively. Note that the column from the left refers to electrodes without PAAcid (only Nafion®), and the one on the right, to sensors containing the polymer



change in the signal corresponding to direct measurement (A treatment) is observed (Fig. 2 a and e), but a 30% increase is evident after a 5-min incubation period in NaCl + Cu²⁺ solution (B treatment, Fig. 2 b and f). On the other hand, from Fig. 2 c and g (C treatment, incubation in the sample with Cu²⁺ and measurement in the absence of the ion), we can infer that during the incubation period, Cu²⁺ is retained by the PAAcid, but not by the Nafion®, since in the former case, the Cu²⁺ signal is observed after changing the solution, but not in the latter. Finally, if the electrode is incubated in NaCl and measured in the presence of NaCl + Cu²⁺ (treatment D), a 20% increase in cathodic current is observed for the electrodes containing PAAcid with respect to electrodes modified only with Nafion®.

Considering these results, to prepare the calibration line ("Calibration curve"), the treatment used was a combination of treatments C and D: after modifying the electrodes with the Nafion® + PAAcid mixture, they were incubated 5 min in 3.5% NaCl (D treatment) and left to dry on air, and then we followed C treatment. These conditions resulted in an improvement in the repeatability with respect to applying C treatment directly, and allow incubating in situ and measuring in controlled solution (see "Electrochemical measurements" and "Visible and infrared spectral characterization").

Visible and infrared spectral characterization

In the preparation of ionic sensors, organic molecular ligands are widely used due to its specific recognition for metals. The interaction between heavy metals and organic ligands can be explained based on the Pearson theory of hard and soft acids and bases (HSAB), in which the soft acids react faster and form stronger bonds with soft bases and vice versa. Thus, the different heavy metal ions tend to react selectively with ligands containing sulfur, oxygen, and/or nitrogen-donorcontaining groups, depending on the surface modification of electrodes. In [21], the authors make use of the fact that at pH higher than approximately 5, the –COO[–] groups from the PAAcid are deprotonated and can therefore bind transition metal cations. Considering this, they used polysulfonepolyacrylic acid blends as ultrafiltration membranes to remove metals from water.

In our system, we proposed the modification of the surface with –COOH groups bearing PAAcid because it is known that this polymer is a good chelating agent for metal cations [22, 23], thus retaining the analyte and increasing the electrochemical signal. The measured visible and infrared spectra are spectroscopic evidence for the mentioned hypothesis.

Visible absorption spectra were measured in solution for 50 mM CuSO₄ in the absence and in the presence of 15 mg/ mL PAAcid (Fig. 3). By adding the polymer, a blue shift of approximately 25 nm was observed, indicating an



Fig. 3 Visible spectra for 50 mM $CuSO_4$ and 50 mM $CuSO_4$ + 15 mg/mL PAAcid. The pH was adjusted to 2 with H_2SO_4 . A blue shift of 25 nm is observed in the presence of the polymer

enhancement in the d orbital splitting due to the complexation of the copper with the polymer –COOH groups [24].

IR spectroscopy in the transmission mode was used to characterize the surface modification and its interaction with copper under several conditions. For this purpose, AgCl windows were modified with the Nafion®-PAAcid mixture, left to dry and incubated for 5 min with 3.5% NaCl or 0.1 M CuSO₄ in 3.5% NaCl.

Figure 4 shows the spectra of Nafion® and the Nafion®-PAAcid matrix. The peaks with wavenumbers between 1200 and 500 cm⁻¹ correspond to Nafion® in its protonated form, and are assigned in Table 2 according to [25]. These peaks do not change upon treatment of the Nafion® to prepare the Nafion®-PAAcid matrix or upon incubation with the aqueous solutions.



Fig. 4 IR spectra of AgCl windows modified with 8 μ L Nafion® or Nafion® + PAAcid mixture. Thirty-two spectra with a resolution of 4 cm⁻¹ were averaged. Air was measured as background

Table 2Infrared spectraassignations

					Pedre I. et al.
Nafion		Polyacrylic acid		Polyacrylic acid + Cu ²⁺	
Wavenumber (cm ⁻¹)	Assignation	Wavenumber (cm ⁻¹)	Assignation	Wavenumber (cm ⁻¹)	Assignation
1212	ν_{as} (CF ₂)	1715–1730	ν (C=O)	1620–1645	ν (C=O, Cu)
1160	$\nu_{s}\left(CF_{2}\right)$	~ 1580	ν_{as} (CO ₂ ⁻)		
1065	ν_{s} (SO ₃ ⁻)				
984	ν_{s} (to C-O-C)				
968 (s)					
634	ω (CF ₂)				

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In the spectrum of the Nafion®-PAAcid matrix (Fig. 4, Table 2), a peak that is not present in the absence of the acid appears at around 1700 cm^{-1} and is assigned to the PAAcid, corresponding to the C=O stretching mode of the carboxylic acid groups [26].

Furthermore, the windows were modified with Nafion® + PAAcid mixtures adjusted to different pH values (3, 6, and 13). In Fig. 5, we present the corresponding IR spectra. It can be seen that as the pH increases well above the typical pK_a value for carboxylic acids (around 4.5), the area of the peak at 1705 cm⁻¹ corresponding to the –COOH moieties decreases and a new peak appears at 1580 cm⁻¹ corresponding to the antisymmetric stretching of the –CO₂⁻. This shift is in accordance with the behavior reported in [27] for the polyacrylic acid-polyacrylate system upon deprotonation.

Figure 6 shows the IR spectra of our systems after being incubated 5 min with NaCl 3.5% or 0.1 M CuSO_4 in 3.5% NaCl. Panel a of Fig. 6 shows the spectra of films prepared at pH = 3, and panel b at pH = 6.

At the lower pH (i.e., 3), before treatment, a signal corresponding to the C=O stretching of the carboxylic acid group at 1718 cm^{-1} can be seen (inset). The position of these bands indicates that the carboxylic moieties form hydrogen-bonded dimers

[28]. Upon incubation with NaCl, the band corresponding to the C=O stretching moves slightly to higher wavenumbers (1728 cm⁻¹). Differently, in the samples incubated with CuSO₄, the band corresponding to the C=O stretching of the carboxylic acid group at 1718 cm⁻¹ diminishes greatly and a new band at 1644 cm⁻¹ appears. This new band can be assigned to the interaction of the carboxylic acid functionalities with the copper ions present in solution, producing the loss of the proton and replacement with a copper ion. This change may form monodentate, bidentate, or bridging structures [27, 29, 30]. Moreover, these results are in accordance with our visible spectra (see above), and in agreement with our hypothesis that the PAAcid is acting as a complexing agent for Cu²⁺ ions.

At higher pH (polymeric mixture at pH 6 or 13), upon incubation with NaCl, the peak corresponding to the stretching of the –COOH disappears. This seems to indicate that the Nafion® loses the PAAcid at higher pH, which can be explained if we consider that the deprotonated form is more soluble in water than the protonated one, and is therefore removed from the film. On the opposite, after incubation with Cu^{2+} , the carboxylate-Cu signal is still observed, implying that the PAAcid is not dissolved in this case. This seems to indicate that the presence of Cu^{2+} and its interaction with the –

Fig. 5 IR spectra of AgCl windows modified with 8 μ L Nafion® + PAAcid mixtures at different pH values. Thirty-two spectra with a resolution of 4 cm⁻¹ were averaged. Air was measured as background. The right panel is a zoom from the left one



Fig. 6 IR spectra for AgCl windows modified with Nafion®-PAAcid mixtures at different pH values: **a** pH 3 and **b** pH 6. The films were measured as prepared and after incubation with 3.5% NaCl or 3.5% NaCl containing 0.1 M CuSO₄. A new film was used for each incubation. Thirty-two spectra with a resolution of 4 cm⁻¹ were averaged. Air was measured as background. Right panels are a zoom from the left ones



COOH moieties of the PAAcid somehow attaches the PAAcid to the Nafion.

Calibration curve

For the analytical determination of copper, square wave voltammograms were carried out at frequency = 8 Hz, step potential = 5 mV, and amplitude = 20 mV. The potential was swept from positive to negative potentials. A calibration curve (Fig. 7) was measured in triplicate in independent experiments under a combination of treatments C and D, that is, the electrodes modified with the Nafion®-PAAcid mixture were incubated for 5 min in 3.5% NaCl, rinsed with water, and left to dry in air. Afterwards, voltammograms were measured using treatment C (incubation in NaCl + Cu and subsequent measurement in NaCl). Preliminary tests showed a strong dependence of the sensitivity of the sensor with the concentration of NaCl, so in the construction of the calibration curve, this must be kept constant, as well as the temperature, due to the adsorption processes involved.

The calibration curve obtained from 3 independent measurements performed per concentration level was $I_{\text{peak}} = (0.16 \pm 0.01) \ \mu\text{A}/\mu\text{M} \ [\text{Cu}^{2+}] + (0.7 \pm 0.3) \ \mu\text{A}, R^2 = 0.9866$, with a limit of detection of 12 μ M, calculated as recommended in [31]. Confidence bands at 95% are shown in green color in Fig.7. The linear range extended up to 50 μ M Cu²⁺. This data makes the sensor useful for its application in drinking water (EPA permissible concentration, 20 μ M [4]). For its use in environmental samples, depending on the sample, a preconcentration step would be necessary.



Fig. 7 Calibration curve for Cu^{2+} ion. **a** Square wave voltammograms. Frequency = 8 Hz, step potential = 5 mV, amplitude = 20 mV. The potential was swept from positive to negative potentials. The electrodes used were modified with Nafion®-containing PAAcid and were used according to a combination of treatments C and D. **b** I_{peak} as a function

Electrodes were tested with the same treatment 1 week after their preparation in 25 μ M Cu²⁺ solution, giving results according to the expected values (mean = 4.3 μ A, SD = 1.3 μ A, n = 5), showing the possibility of being prepared previously to their use in, for example, field measurements.

Selectivity study

Glassy carbon electrodes (7 mm²) were modified with 0.8 μ L of Nafion®-PAAcid mixture and incubated 5 min in solutions of Cu²⁺, Cd²⁺, Fe³⁺, Pb²⁺, or Zn²⁺ (200 to 1000 μ M in NaCl 3.5%). Afterwards, square wave voltammograms were measured in the same conditions as in "Calibration curve" but in a broad potential window. As can be seen in Fig. 8, only Cu²⁺ gives a signal, indicating that the surface in the present conditions is selective for this cation.

Application to real samples

Affinity between the modified surface and other components in natural matrices could affect the performance of this sensor. A real seawater sample was collected in the town of Villa Gesell (Buenos Aires Province, Argentina, 37° 15' 20" S 56° 58' 05" W) and a real river water was collected in the Ensenada Port (34° 51' 40.73" S 57° 53' 04.58" W). Drinking water from the public network was collected from our university (Ciudad Universitaria, Buenos Aires). All samples were stored at -18 °C until their use. All of them contained less than 0.06 µM of copper which is suitable for this study. The samples were filtered using 0.22-µM pore diameter membranes and spiked with 10, 20, 30, or 50 µM Cu^{2+} for seawater; 20, 30, 50, 75, and 100 μ M for river water; and 10, 20, 30, 40, or 50 µM for drinking water. Afterwards, the same method as for the calibration curve was applied (incubation in sample, measurement in 3.5% NaCl). The reduction current values as function of copper concentration were



of Cu²⁺ concentration. Curve equation: $I_{\text{peak}} = (0.16 \pm 0.01) \ \mu\text{A}/\mu\text{M}$ [Cu²⁺] + (0.7 ± 0.3) μ A, $R^2 = 0.9866$. The linear range goes from 0 to 50 μ M Cu²⁺ and the limit of detection is 12 μ M. The error bars correspond to the standard deviation from 3 independent measurements

evaluated in seawater and river and drinking water. For seawater, an average sensitivity $(0.040 \pm 0.001) \ \mu A/\mu M$ was measured ($R^2 = 0.9961$, limit of detection = 12 μ M). For river water, the corresponding values are sensitivity = $(0.008 \pm 0.001) \ \mu A/\mu M$, $R^2 = 0.9300$, limit of detection = 50 μ M, while for drinking water, the values are: sensitivity = $(0.20 \pm 0.02) \ \mu A/\mu M$, $R^2 = 0.9812$, limit of detection = 18 μ M. All three data sets are shown in Fig. 9.

The response of the sensor in the natural water samples reveals its strong sensitivity dependence with the matrix. In seawater, this effect can be related with the concentration of sodium chloride as mentioned in the "Calibration curve" section. The employed sample of river water is from Río de la Plata, which is characterized by high concentration of organic and inorganic compounds [32]. These compounds can act as



Fig. 8 Square wave voltammograms for the selectivity study. Frequency = 8 Hz, step potential = 5 mV, amplitude = 20 mV. The potential was swept from positive to negative potentials. Glassy carbon electrodes (7 mm²) were modified with 0.8 μ L of Nafion®-PAAcid mixture and incubated 5 min in solutions containing the corresponding cation (3.5% NaCl), after which, the square wave voltammograms were measured



Fig. 9 Calibration curves in real samples: seawater from the town of Villa Gesell (37° 15' 20" S 56° 58' 05" W), river water collected in the Ensenada Port (34° 51' 40.73" S 57° 53' 04.58" W), and drinking water from the public network from our university. All samples contained less than 0.06 μ M of copper which is suitable for this study. The samples were filtered using 0.22-µM pore diameter membranes and spiked with 10, 20, 30, or 50 μM Cu^{2+} for seawater; 20, 30, 50, 75, and 100 μM for river water: and 10, 20, 30, 40, or 50 µM for drinking water. The different responses for natural samples can be attributed to the high concentration of organic and inorganic compounds of the Río de la Plata. The calibration curve for seawater is $I_{\text{peak}} = (0.040 \pm 0.001) \ \mu\text{A}/\mu\text{M}$ $[Cu^{2+}] + (0.32 \pm 0.03) \mu A$, $R^2 = 0.9961$, LOD = 12 μM . For river water, the curve is $I_{\text{peak}} = (0.008 \pm 0.001) \ \mu\text{A}/\mu\text{M} \ [\text{Cu}^{2+}] + (0.35 \pm 0.06) \ \mu\text{A}$, $R^2 = 0.9300$, LOD = 50 μ M. For drinking water, the curve is $I_{\text{peak}} = (0.20 \pm 0.01) \ \mu\text{A}/\mu\text{M} \ [\text{Cu}^{2+}] + (0.3 \pm 0.4) \ \mu\text{A}, \ R^2 = 0.9812,$ $LOD = 18 \mu M$

complexing agents and reduce the copper available to react with the sensor surface. Because of this, the figures of merit get considerably worse and the linear dynamic range of sensor operation seems to be modified. So in this type of samples, it would be necessary to evaluate the use of this sensor with the standard addition method for the determination of free copper and perform a complete mineralization of the sample if the total copper concentration is required. In drinking water samples, on the other hand, the sensors can be applied as prepared.

Conclusions

In this work, it has been demonstrated that a Nafion® polymeric matrix can be used to modify graphite screen-printed electrodes with polyacrylic acid as a recognizing agent for Cu^{2+} in natural water samples. The proposed polymeric matrix and its interaction with copper were studied physicochemically.

The PAAcid is easily dissolved in the matrix and the resulting mixture can be applied to the electrodes by drop casting, thus giving a simple modification procedure. Therefore, this modification process can be considered as a convenient alternative to other modification methods as covalent linkage, layer by layer polyelectrolyte assembling, or polymer brushes. The Nafion®-PAAcid matrix resulted to be stable for determinations in samples with high salinity. Furthermore, this platform could be used to modify commercial screen-printed electrodes.

The analytical determination was made with the technique of square wave voltammetry, and the sensor was useful for concentrations in the range of 50 μ M and its potential use in real samples (sea, river, and drinking water from the public network) was evaluated. It was postulated that the polyacrylic acid can act as a chelating agent for the analyte. This assumption was supported by visible and IR spectroscopy.

The modified electrodes are inexpensive and easy to prepare and can be transported and used in the field. Measurements are fast, involving only a 5-min incubation step. These properties are great advantages over the reference method (ICP).

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References

- Krstić V, Urošević T, Pešovski B. A review on adsorbents for treatment of water and wastewaters containing copper ions. Chem Eng Sci. 2018;192:273–87. https://doi.org/10.1016/j.ces.2018.07.022.
- Ullah N, Mansha M, Khan I, Qurashi A. Nanomaterial-based optical chemical sensors for the detection of heavy metals in water: recent advances and challenges. TrAC Trends Anal Chem. 2018;100:155–66. https://doi.org/10.1016/j.trac.2018.01.002.
- Khairy GM, Duerkop A. Dipsticks and sensor microtiterplate for determination of copper (II) in drinking water using reflectometric RGB readout of digital images, fluorescence or eye-vision. Sensors Actuators B Chem. 2019;281:878–84. https://doi.org/10.1016/j. snb.2018.10.147.
- Song P, Xiang Y, Wei R, Tong A. A fluorescent chemosensor for Cu²⁺ detection in solution based on aggregation-induced emission and its application in fabricating Cu²⁺ test papers. J Lumin. 2014;153:215–20. https://doi.org/10.1016/j.jlumin.2014.03.030.
- Justino CIL, Freitas AC, Duarte AC, Santos TAPR. Sensors and biosensors for monitoring marine contaminants. Trends Environ Anal Chem. 2015;6–7:21–30. https://doi.org/10.1016/j.teac.2015. 02.001.
- Stumm W, Morgan JJ. Aquatic chemistry: chemical equilibria and rates in natural waters. 3rd ed. New York: Wiley; 1996.
- Rauch JN, Graedel TE. Earth's anthrobiogeochemical copper cycle: COPPER CYCLE. Glob Biogeochem Cycles. 2007;21:n/a-n/a https://doi.org/10.1029/2006GB002850.
- dos Santos Carlos F, Nunes MC, De Boni L, Machado GS, Nunes FS. A novel fluorene-derivative Schiff-base fluorescent sensor for copper(II) in organic media. J Photochem Photobiol A Chem. 2017;348:41–6. https://doi.org/10.1016/j.jphotochem.2017.08.022.

- Santos IC, Mesquita RBR, Rangel AOSS. Micro solid phase spectrophotometry in a sequential injection lab-on-valve platform for cadmium, zinc, and copper determination in freshwaters. Anal Chim Acta. 2015;891:171–8. https://doi.org/10.1016/j.aca.2015. 08.021.
- Frag EY, Mohamed MEB, Fahim EM. Application of carbon sensors for potentiometric determination of copper(II) in water and biological fluids of Wilson disease patients. Studying the surface reaction using SEM, EDX, IR and DFT. Biosens Bioelectron. 2018;118:122–8. https://doi.org/10.1016/j.bios.2018.07.024.
- Herzog G, Moujahid W, Twomey K, Lyons C, Ogurtsov VI. Onchip electrochemical microsystems for measurements of copper and conductivity in artificial seawater. Talanta. 2013;116:26–32. https:// doi.org/10.1016/j.talanta.2013.04.057.
- Kayarkatte MK, Delikaya Ö, Roth C. Polyacrylic acid-Nafion composites as stable catalyst support in PEM fuel cell electrodes. Mater Today Commun. 2018;16:8–13. https://doi.org/10.1016/j.mtcomm. 2018.02.003.
- Kefala G, Economou A, Voulgaropoulos A. A study of Nafioncoated bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry. Analyst. 2004;129:1082. https:// doi.org/10.1039/b404978k.
- Papadopoulou NA, Florou AB, Prodromidis MI. Sensitive determination of iron using disposable Nafion-coated screen-printed graphite electrodes. Anal Lett. 2018;51:198–208. https://doi.org/10. 1080/00032719.2017.1302464.
- Vlassiouk I, Takmakov P, Smirnov S. Sensing DNA hybridization via ionic conductance through a nanoporous electrode. Langmuir. 2005;21:4776–8. https://doi.org/10.1021/la0471644.
- González G, Priano G, Günther M, Battaglini F. Mass transport effect of mesoscopic domains in the amperometric response of an electroactive species: modeling for its applications in biomolecule detection. Sensors Actuators B Chem. 2010;144:349–53. https:// doi.org/10.1016/j.snb.2008.11.006.
- El-Hashani A, Toutianoush A, Tieke B. Layer-by-layer assembled membranes of protonated 18-azacrown-6 and polyvinylsulfate and their application for highly efficient anion separation. J Phys Chem B. 2007;111:8582–8. https://doi.org/10.1021/jp0688052.
- Macanás J, Ouyang L, Bruening ML, Muñoz M, Remigy J-C, Lahitte J-F. Development of polymeric hollow fiber membranes containing catalytic metal nanoparticles. Catal Today. 2010;156: 181–6. https://doi.org/10.1016/j.cattod.2010.02.036.
- Jain P, Baker GL, Bruening ML. Applications of polymer brushes in protein analysis and purification. Annu Rev Anal Chem. 2009;2: 387–408. https://doi.org/10.1146/annurev-anchem-060908-155153.
- Priano G, González G, Günther M, Battaglini F. Disposable gold electrode array for simultaneous electrochemical studies. Electroanalysis. 2008;20:91–7. https://doi.org/10.1002/elan. 200704061.
- 21. Mbareck C, Nguyen QT, Alaoui OT, Barillier D. Elaboration, characterization and application of polysulfone and polyacrylic acid

blends as ultrafiltration membranes for removal of some heavy metals from water. J Hazard Mater. 2009;171:93–101. https://doi. org/10.1016/j.jhazmat.2009.05.123.

- Bala T, Prasad BLV, Sastry M, Kahaly MU, Waghmare UV. Interaction of different metal ions with carboxylic acid group: a quantitative study. J Phys Chem A. 2007;111:6183–90. https:// doi.org/10.1021/jp067906x.
- Mehandzhiyski AY, Riccardi E, van Erp TS, Koch H, Åstrand P-O, Trinh TT, et al. Density functional theory study on the interactions of metal ions with long chain deprotonated carboxylic acids. J Phys Chem A. 2015;119:10195–203. https://doi.org/10.1021/acs.jpca. 5b04136.
- 24. Basolo F, Johnson R. Coordination Chemistry. St Lucie Press; 1986.
- Kosseoglou D, Kokkinofta R, Sazou D. FTIR spectroscopic characterization of Nafion®–polyaniline composite films employed for the corrosion control of stainless steel. J Solid State Electrochem. 2011;15:2619–31. https://doi.org/10.1007/s10008-010-1241-3.
- Li W, Zhao H, Teasdale PR, John R, Zhang S. Synthesis and characterisation of a polyacrylamide–polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd. React Funct Polym. 2002;52:31–41. https://doi.org/10.1016/S1381-5148(02) 00055-X.
- Hu H, Saniger J, Garcia-Alejandre J, Castaño VM. Fourier transform infrared spectroscopy studies of the reaction between polyacrylic acid and metal oxides. Mater Lett. 1991;12:281–5. https:// doi.org/10.1016/0167-577X(91)90014-W.
- Lin-Vien D, editor. The handbook of infrared and raman characteristic frequencies of organic molecules. Boston: Academic Press; 1991.
- Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds. 6th ed. Hoboken: Wiley; 2009.
- 30. Smith EL, Alves CA, Anderegg JW, Porter MD, Siperko LM. Deposition of metal overlayers at end-group-functionalized thiolate monolayers adsorbed at Au. 1. Surface and interfacial chemical characterization of deposited Cu overlayers at carboxylic acidterminated structures. Langmuir. 1992;8:2707–14.
- 31. British Standard ISO 11843-2:2000, Capability of detection, Part 2: Methodology in the linear calibration case.
- Tatone LM, Bilos C, Skorupka CN, Colombo JC. Trace metal behavior along fluvio-marine gradients in the Samborombón Bay, outer Río de la Plata estuary, Argentina. Cont Shelf Res. 2015;96: 27–33. https://doi.org/10.1016/j.csr.2015.01.007.

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