



Simple Electrochemical Detection Method Employing a Hydrogel Soft Matrix: Application in Tap Water

María V. Martinez, Rusbel Coneo Rodriguez, Mariano M. Bruno, ^{ORCID} Diego F. Acevedo,^z and Cesar A. Barbero

Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados (IITEMA), Universidad Nacional de Río Cuarto (UNRC)- Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), X5804ZAB, Río Cuarto (Córdoba), Argentina

The proposed method implies the electrochemical detection of an analyte preloaded in a hydrogel. In order to evaluate the potential application of this method, arsenic detection in tap water was performed. Polymeric hydrogels bearing cationic groups poly(N-isopropylacrylamide)-co-3-(acrylamidopropyl)trimethylammonium chloride were used to sorb arsenic ions, at basic pH, from the real and synthetic stock samples. The concentration of arsenic was electrochemically determined using the loaded hydrogel and a modified glassy carbon electrode. Employing a cationic hydrogel, the peak current for the arsenic oxidation was ca. 8 times higher than the peak current measured using poly(N-isopropylacrylamide), a neutral hydrogel, indicating a strong electrostatic interaction between the polymeric cationic groups and arsenite anions. By using this method, values of arsenic comparable to those measured by Atomic Absorption Spectroscopy were obtained for tap water of small cities in Argentina. These results suggest that this new and easy method is suitable to sense a threshold limit of arsenic in real samples since the features of the hydrogel allow the arsenite loading into the matrix. Besides the cationic hydrogels could be employed to sampling on-field and to build a portable analysis system.

© 2018 The Electrochemical Society. [DOI: 10.1149/2.0031816jes]

Manuscript submitted September 25, 2018; revised manuscript received November 7, 2018. Published November 27, 2018.

Polymeric hydrogels are a group of materials which could hold large amounts of water in their three-dimensional due to the hydrophilic nature of the polymer chains and the high flexibility of the polymer matrix. This property makes them suitable for environmental applications where species in aqueous solutions could interact with functional groups of the polymeric chains. Fixed charges in the gel can be easily incorporated by copolymerization of monomers bearing selected functional groups which can interact specifically with different compounds of interest.¹ For example, it has been demonstrated that the hydrogels containing fixed positive charges interact and retain anionic arsenic species,² a cationic hydrogel can remove up to 99.7% As(V) from a 50 ppm solution of As(V) in 360 min. However, the application of this material to sense arsenic has not been developed.

In previous research works, Martinez et al.^{3,4} developed a simple experimental setup where a hydrogel matrix is used to load redox active substances, which were characterized by employing electrochemical techniques. The results showed that the redox probes are present as dilute solutions and the hydrogel dimensions fulfill the semi-infinite diffusion boundary conditions, therefore the data analysis can be performed using the theoretical framework for electrochemical measurements in liquid solvents.^{3,4} Furthermore, it was proved that the use of nanoporous material facilitates its handling and allows filtering out of large species (e.g. proteins or polysaccharide).⁵ Consequently, this kind of materials could be used to adsorb analytes not only from water but also from complex solutions such as milk.⁵

The arsenic is one of the elements that the World Health Organization (WHO) considers more worrying for public health.⁶ Several approaches to arsenic removal including oxidation, reduction, precipitation, ion exchange, adsorption, lime treatment, solid-liquid separation, physical exclusion, biological removal processes and reverse osmosis has been developed.^{7,8} However, previous to the applied removal treatments is extremely important to develop a quick and effective method of arsenic determination. Arsenic and arsenic compounds have been classified by the International Agency for Research on Cancer (IARC) as IARC Group 1 (carcinogenic to humans).⁹ Arsenic contamination of soil and groundwater is widespread in the world. In our country, Argentina, arsenic, and arsenic compounds are present in the Pampa plains,^{10,11} where the most rural population is located (>2.000.000 inhabitants).^{12,13} The presence of this contaminant is mainly due to the deposition of ashes from volcanic events along the earth history. A complication in isolated or rural places is difficult to execute arsenic

periodical determinations in tap water and to generate procedures to decontaminate the water. Arsenic occurs in natural waters mainly as inorganic trivalent arsenite (As(III)) and pentavalent arsenate (As(V)), however, it can be found in other forms including soluble, particulate, and organic bound species.¹⁴ The arsenic maximum reference level of 10 ppb has been worldwide established. Even though this is the optimum level, WHO reported that only when the concentration is higher than 50 ppb the arsenic produces adverse effects on health occurs.

Therefore, several organizations in Argentina (such as Subsecretaría de Recursos Hídricos (SSRH)) established 50 ppb as the arsenic maximum level in drinking water.¹⁵

Nowadays, the presence of arsenic species in food and/or drinking water is a matter of concern.¹⁶ According to scientists involved in research on arsenic contamination, there has never been any easy routine to test arsenic levels in real samples. All these situations may perhaps avoid if the arsenic content in water or food could be determinate in a fast and easy way using a portable device. Some of the well-known analytical methods used for the determination of arsenic inorganic include inductively-coupled plasma mass spectrometry (ICP-MS), hydride-generation atomic absorption and emission spectrometry (HG-AAS/AES), atomic fluorescence spectrometry (AFS), and high-performance liquid chromatography (HPLC).¹⁷ However, these methods require expensive and sophisticated instruments, high operating costs, and complicated sample preparation processes (e.g. digestion or clean-up steps). Additionally, as these techniques are time-consuming, they may not be suitable for routine and on-field analysis. Electroanalytical techniques have been demonstrated to be a promising alternative to replace conventional methods due to their simple instrumentation, high sensitivity, selectivity, ease of use, miniaturization, short analysis time, minimal sample pretreatment, and portability.¹⁸ In this regard, stripping voltammetry has been implemented for the arsenic determination using different metal electrodes (Hg, Pt, Au).^{19,20} However, there are often problems associated with the formation of an intermetallic complex with arsenic. These drawbacks are related to the low electron transfer kinetics, low stability over a wide range of solution composition, and poor reproducibility²¹ of the electrode surfaces between each measurement.

A large number of research studies have been devoted to the determination of heavy metal ions because the exposure to low concentrations of these metal ions represents a risk of serious adverse human health effects. In this important research area, modified electrodes have attracted considerable attention as an electrochemical low-cost method to the sensitive detection of a variety of analytes. Determination of lead, cadmium, copper, arsenic,

^zE-mail: dacevedo@exa.unrc.edu.ar; mbruno@exa.unrc.edu.ar

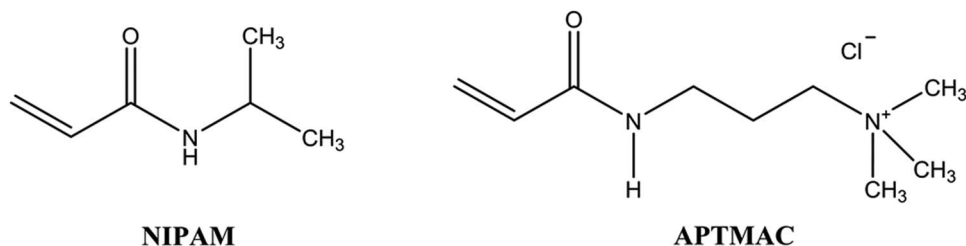


Figure 1. Chemical structure of the monomers NIPAM and APTMAC.

mercury and chromium by modified electrodes were successfully applied in environmental resources.^{22–27} Regards electrochemical arsenic detection nanostructured materials such as noble metal, metal oxide nanoparticle-modified electrodes,^{28–30} carbon nanoparticle-modified electrodes (carbon nanotube/graphene),^{31,32} and bimetallic nanoparticle-modified electrodes³³ have been demonstrated good sensibility due to their catalytic properties and roughening of the conductive sensing interface. Recently, we have demonstrated that modified electrodes with cobalt oxide nanoparticles^{34,35} present excellent performance toward arsenic oxidation over a wide pH range (5 to 11). Based in the precedent antecedents, taking the advantage of the electrochemical techniques (involving modified electrodes with cobalt oxide nanoparticles)^{36,37} and the gels ability to load compounds, in this research work an effortless method to detect arsenic in real samples with high sensitivity is described. Moreover, using the proposed method it will be possible to build a portable device that would make a new on-field diagnosis technique. The proposed method to arsenic sensing involves the analyte loading into a polymeric crosslinked cationic matrix (hydrogel) by one sorption step. After that, the gel is placed into the electrochemistry cell and the working electrode is pressed slightly onto the gel until reaching the physical contact. The cell is filled with electrolyte and then the electrochemistry signal is recorded. A glassy carbon electrode modified with cobalt oxide nanoparticles was used as a working electrode to sense arsenic. Three samples of tap water, from different Argentina small cities (Venado Tuerto (Santa Fe), Laboulaye (Córdoba) and Sampacho (Córdoba)) were analyzed.³⁸ The measured values employing the proposed technique are in agreement with those measured by Atomic Absorption Spectrometry validating the method.

Experimental

Materials.—N-isopropylacrylamide (NIPAM, Scientific Polymer Products) and (3-acrylamidopropyl)trimethylammonium chloride (APTMAC) were used as monomers. N,N-methylenebisacrylamide (BIS), N,N,N',N'-tetramethylethylenediamine (TEMED) and ammonium peroxydisulfate (APS) were purchased from Aldrich. Millipore (18.2 MΩ · cm) purified water was used to prepare the solutions. The pH 9.6 buffer solution (osmotic pressure of ca. 1.3 atm) was prepared using sodium hydrogen carbonate (0.05 M NaHCO₃) and sodium hydroxide (0.1 M NaOH). Sodium arsenite (NaAsO₂, Aldrich) was used to prepare arsenic stocks solutions.

Cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, Aldrich) and sodium acetate anhydrous (CH₃COONa, Cicarelli) and the other reagents used were of analytical grade.

Synthesis of hydrogels.—Poly(N-isopropylacrylamide-co-3-(acrylamidopropyl)trimethylammonium chloride) (PNIPAM-co-50%APTMAC) hydrogel was synthesized via free radical copolymerization of NIPAM (1 M) with APTMAC (1 M). The monomeric chemical structures of the hydrogels are shown in Figure 1.

The total monomer concentration was 2 M and BIS was used as a crosslinker. The radical polymerization was initiated by the redox system composed by APS and TEMED. The monomers, the crosslinker (0.04 M BIS) and the APS (4.4 mM) were placed in a tube and

water was added until a final volume of 4 mL was reached. Then, the solution was deoxygenated by bubbling with N₂ gas. Finally, TEMED (0.13 mM) was added to start the polymerization. Once the gelation was completed, the hydrogels were immersed in distilled water at room temperature for 48 h. The water was renewed several times in order to remove the unreacted compounds. Homopolymeric hydrogels of NIPAM (0.5 M) and APTMAC (0.5 M) were also synthesized employing the same synthesis conditions explained for the copolymers.

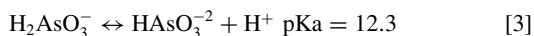
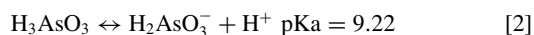
The synthesized hydrogels, Poly(N-isopropylacrylamide) (PNIPAM), Poly (3-(acrylamidopropyl)trimethylammonium chloride) (PAPTMAC) and PNIPAM-co-50%APTMAC, were characterized by FTIR-ATR spectroscopy (Perkin Elmer, Spectrum two).

Properties of hydrogel matrix: swelling kinetic and swelling capacity in equilibrium.—Dry hydrogel samples previously weighed were placed in water and buffer solution (pH 9.6) at room temperature. Each certain lapse of time the gels were removed from the solution, superficially dried with tissue paper and weighed in an analytical balance. The swelling percentage (%Sw) was calculated as a function of time according to the Equation 1:

$$\%Sw = (W(t) - W_0) / W_0 \cdot 100 \quad [1]$$

where $W(t)$ represents the weight of swollen hydrogel at a given time and W_0 is the weight of the dry hydrogel. Graphics of %Sw vs time were achieved to analyze the swelling kinetics. The swelling percentage in equilibrium (%Sw_{eq}) was calculated by measuring the hydrogel weight until constant weight (W_{eq}).

Arsenite sorption process.—A dried hydrogel was immersed in arsenite aqueous solution. The 50 ppb (0.67 μM) and 100 ppb (1.33 μM) arsenic stock solutions were made using a buffer solution pH 9.6. At this pH value, the arsenic species are negatively charged, according to the corresponding values of pKa (see Equations 2 and 3).³⁹



Then, the gel was allowed to swell, taking the outer solution, until reaching the equilibrium swelling (24 hours). The anions were loaded inside the polymeric matrix by electrostatic interaction. Once the gel was loaded with H₂AsO₃⁻, the arsenic loaded PNIPAM-co-50%APTMAC hydrogel was poured into the electrochemistry cell. The cell was filled with the electrolyte (free arsenic buffer solution, pH 9.6), and the electrochemical detection of arsenic was carried out. The same procedure was applied to a neutral hydrogel (PNIPAM), and its capacity to sense arsenic was also tested.

Tap water samples from the cities of Sampacho (Córdoba, Argentina), Laboulaye (Córdoba, Argentina) and Venado Tuerto (Santa Fe, Argentina) were analyzed for the arsenic content. All samples were conditioned at pH 9.6. Then, cationic hydrogels were swelled in the samples of the tap water and the electrochemical analysis was performed without extra-treatments.

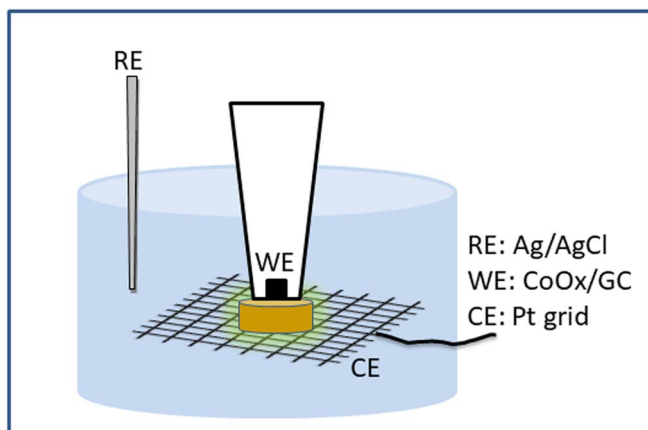


Figure 2. Schematic representation of the set-up used to detect arsenic inside of the hydrogel by electrochemical techniques. RE, reference electrode; WE, the working electrode; CE, counter electrode.

Electrochemistry measurements.—Cobalt oxide film modified glassy carbon electrode.—The arsenic sensing was carried out using cyclic voltammetry (CV). The CV was performed using a glassy carbon disc (GC) electrochemically modified with cobalt oxide nanoparticles (CoOx/GC)⁴⁰ as the working electrode (WE). In order to fabricate the WE a GC electrode (3 mm diameter) was cycled (between -0.4 V and 1.0 V vs Ag/AgCl at 100 $\text{mV} \cdot \text{s}^{-1}$) in a solution containing 0.01 M CoCl_2 and 0.1 M CH_3COONa (pH 7). A platinum (Pt) wire was used as a counter electrode and a Ag/AgCl (KCl sat. solution) electrode as a reference (RE).³⁵ The electrode was cycled for 15 cycles in order to obtain the modified electrode. The electrodeposited cobalt oxide film on GC electrode were characterized by scanning electron microscopy (SEM) (Carl Zeiss-EVOMA10) at low vacuum and low field and by atomic force microscopy (AFM) (Agilent Technologies-SPM model 5500) working in acoustic mode, using a probe (Micromasch, HQ:XSC11/A1 BS) with a cantilever resonance frequency and force constant of 350 kHz and 42 $\text{N} \cdot \text{m}^{-1}$, respectively. All the AFM images were visualized and analyzed using Gwyddion v2.39 free software for scanning probe microscopy data processing.

Arsenic electrochemical detection.—For arsenic electrochemical sensing, a cobalt oxide/GC electrode was employed as a working electrode. Previous research work reported that this modified electrode has a low detection limit of arsenic and its electrochemical response does not suffer significant interference by several substances, such as Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , PO_4^{3-} , Cu^{2+} , Bi^{3+} , Sn^{2+} , Cr^{3+} , Pb^{2+} , Sb^{3+} , Hg^{2+} and Zn^{2+} , that could coexist in the sample with As(III).³⁴ To assure a uniform potential field, a Pt grid below the gel was placed as the counter electrode (CE). An Ag/AgCl (KCl sat. solution) reference electrode was placed inside a glass Luggin capillar. A scheme of the set-up is shown in Figure 2. In order to perform the electrochemical determinations, a hydrogel (PNIPAM-co-50%AMPTAC) piece preloaded with arsenic was located on Pt grid (see Figure 2). Then, the WE was gently pressed onto the hydrogel and the cell was filled with the electrolyte solution (buffer pH 9.6). Several tests were carried out and it was determined that there is any effect of pressure on the hydrogel, once a clear contact between the electrode and the WE was reached.

The electrochemical experiments were performed using a computer-controlled potentiostat (Autolab PGSTAT30, Ecochemie). Cyclic voltammetry experiments were carried between 0.65 V and 1.1 V at 10 $\text{mV} \cdot \text{s}^{-1}$ scan rate. The measurements in solution (absence of the gel) and using the preload hydrogel were performed in the same electrochemical conditions. The current was expressed in current density values by dividing of glassy carbon electrode area.

Results and Discussion

Physicochemical properties of the polymeric hydrogels.—FT-IR (ATR) spectroscopy.—In order to identify the functional groups and characterize the polymer the IR spectra of the PNIPAM-co-50%APTMAC copolymer (Figure 3A), the respective homopolymers PNIPAM (Figure 3B) and PAPTMAC (Figure 3C) were performed.

As it can be observed in the spectrum all the analyzed gels contain secondary amide groups showing a N–H characteristic stretching band at 3650 – 3100 cm^{-1} , while the carbonyl stretching ($\text{C}=\text{O}$, the amide Band I) is observed at 1655 – 1635 cm^{-1} .⁴¹ The amide Band II for secondary amides is due to the coupling of N–H bending and C–N stretching and appears at 1550 – 1540 cm^{-1} . Also, a weak band appears at 3100 – 3060 cm^{-1} which is an overtone of the amide Band II. Moreover, the symmetric and asymmetric stretching of $-\text{CH}_3$ and $-\text{CH}_2$ groups at 2972 cm^{-1} and 2926 cm^{-1} , respectively, have also been identified. The FT-IR spectra of the homopolymers display different bands, PNIPAM presents two peaks at 1173 cm^{-1} and 1130 cm^{-1} due to the isopropyl group presence (no-showed). On the other hand, PAPTMAC has two characteristics peaks at 968 y 915 cm^{-1} that can be assigned to the quaternary ammonium ions,⁴² and also two bands at 1265 cm^{-1} and 1208 cm^{-1} due to the pendant quaternary amine (no-showed). An effective copolymerization can be determinate by FT-IR since Figure 3A shows the bands of the functional groups present of each monomer units.

Swelling characteristics.—The swelling of the studied hydrogels is an important feature to know because a less swollen of the hydrogel indicates a more compact material and, probably this material will retain a very small amount of external solution. Therefore, not only the concentration of the analyte will be small, but also the diffusion coefficient (D) of the analyte inside the polymeric matrix will decrease.³ This undesirable characteristic should also decrease the oxidation current during the electrochemical measurements.⁴³

In Figure 4 the PNIPAM and PNIPAM-%50APTMAC hydrogels swelling kinetics in water a buffer solution (pH 9.6) are shown.

The data were fitted by a first-order kinetics Equation 4.⁴⁴

$$\%Sw(t) = \%Sw_{eq}(1 - e^{-ks.t}) \quad [4]$$

Where ks is the rate constant of the pseudo-first-order swelling model. The values of ks and swelling percentage in equilibrium ($\%Sw_{eq}$) were obtained from the fitting and are shown in Table I.

It can be seen in Figure 4 and Table I that the swelling rate (ks) value of the cationic hydrogel is larger than the neutral hydrogel. This behavior is characteristic of polyelectrolyte based hydrogels (called superhydrophylic) where the fixed charges in its structure create an additional driving force for the inlet of water molecules. The osmotic pressure induces the water intake and the hydrogel swelling. The equilibrium swelling ($\%Sw_{eq}$) in the buffer solution was significantly smaller than that measured in water. This is due to the difference of osmotic pressure between the cationic polymeric gel and the surrounding solvent is higher in the buffer solution than in water. These changes in swelling as a result of osmotic pressure have been previously reported.^{45,46} Lukas Arens et al.⁴⁷ developed an osmotic engine based on osmotic forces. Poly(acrylic acid)-based hydrogels can swell up to 100 – 1000 times their own weight in desalinated water. As the swelling is about a factor of 2 – 12 lower in seawater-like saline solutions (4.3 wt% NaCl) than in deionized water, cyclic swelling, and shrinking can potentially be used to move a piston in an osmotic motor. Moreover, the faster swelling rate is also associated with a smaller elastic force due to a lower viscosity of the hydrogel matrix. Indeed, when the gels are swollen in buffer solution the ks values are similar than the gels swollen in water (Table I), probably because the viscosity does not change significantly.

Generation of the modified electrode to detect arsenic.—In order to prepare the working electrode, the electrodeposition of a cobalt oxide film on GC electrode was performed.³⁵ The cobalt oxide deposition on the electrode surface produced a current increasing during

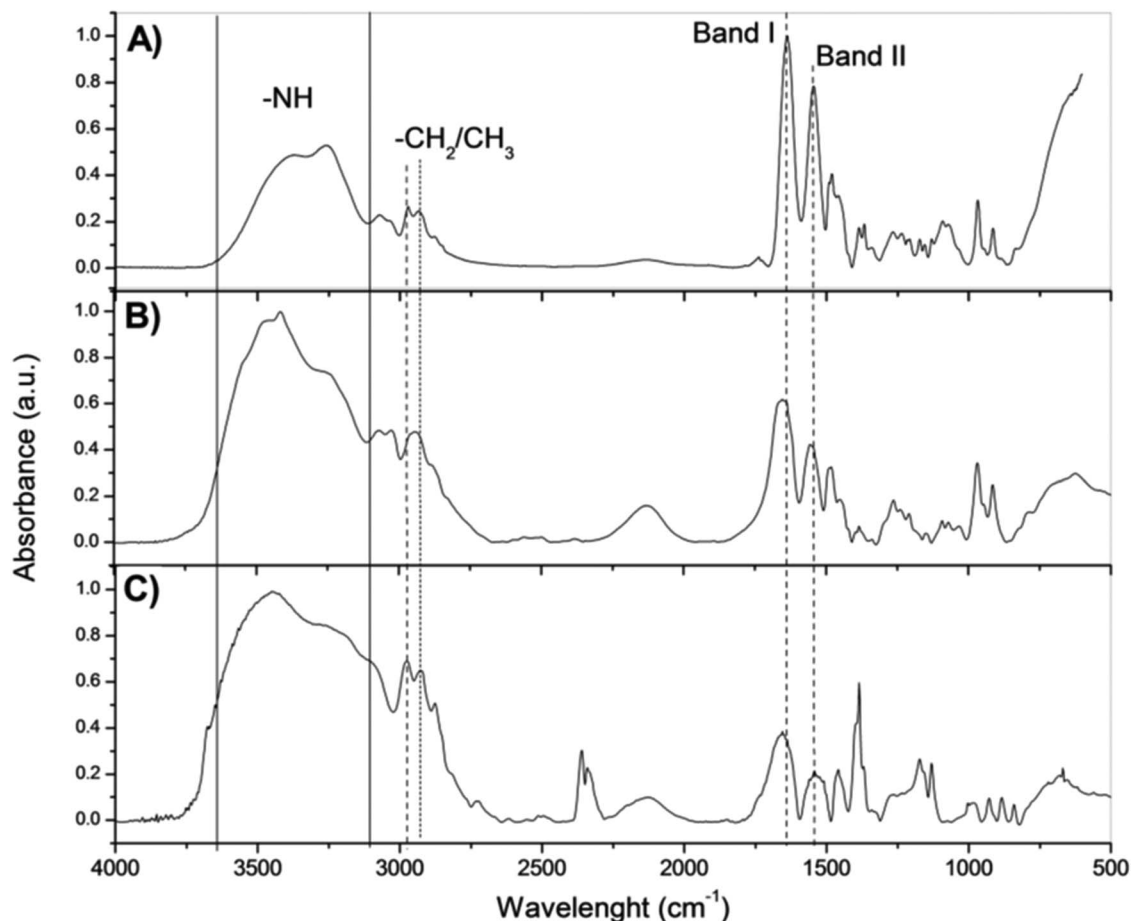


Figure 3. FT-IR (ATR) spectra of: A) PNIPAM-co-50%APTMAC, B) PNIPAM and C) PAPTMAC.

electrochemical cycling by oxide layer growth as can be observed in Figure 5A. At the anodic scan, the oxidation of cobalt ions (Co^{2+}) produces CoO_x species, such as $\text{Co}(\text{OH})_3$, CoOOH and Co_3O_4 which are insoluble at the working pH 7.0 and are deposited on the electrode surface.^{34,48,49} The electrode was removed from the electrochemical cell and the electrode surface was washed gently with ultrapure water and immersed again in the cell filled with the electrolyte (buffer, pH 9.6), in cobalt absence. The cyclic voltammogram shows two reversible peaks that correspond to the oxidation of different cobalt oxide species present on the modified electrode. The peak I correspond to the conversion of $\text{Co}(\text{OH})_2$ to Co_3O_4 , and the peak II is attributed to the oxidation of Co_3O_4 to CoOOH (Figure 5B).^{50,51} The cathodic peaks correspond to the reduction of the different cobalt oxides.

Also, the morphology of the electrodeposited cobalt oxide nanostructures was characterized by scanning electron microscopy and atomic force microscopy. The SEM and AFM images confirm the presence of cobalt oxide film on the GC electrode (See Figure 5C and D). In these micrographs, it can be seen that the electrode surface was completely covered with uniform cobalt oxide particles. Also, the AFM image suggests that the built film presents a thickness not greater than 13 nm.

The electrochemical response of arsenic in solution.—The determination of arsenic was evaluated using the CoO_x/GC electrode by cyclic voltammetry. Figure 6 shows the electrochemical experiments performed in absence, 50 ppb and 100 ppb of arsenic concentration. The electrochemical response of our modified electrode, showed an increasing in the peak current in presence of arsenic, respect to blank (in absence of As), as a consequence of electro-oxidation of arsenic

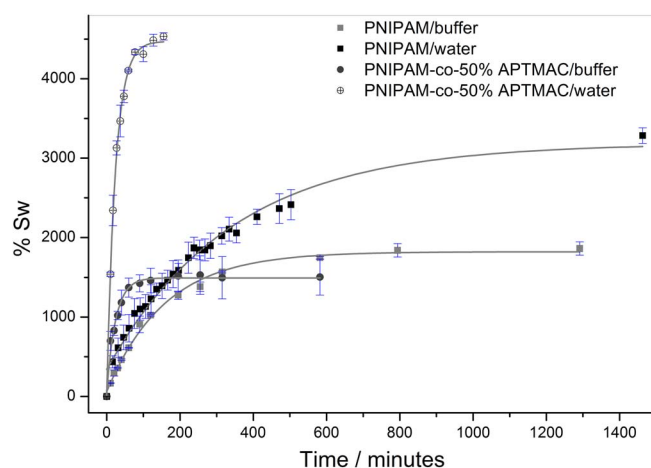


Figure 4. PNIPAM and PAPTMAC-co-50%APTMAC hydrogels swelling kinetics in water and in buffer solution pH 9.6.

(III) to arsenic (V).^{34,35} The oxidation peak for arsenic was observed at ca. 1.03 V (vs Ag/AgCl) (Figure 6).

The results show that the obtained modified electrode has a similar response to those reported by other authors in aqueous solutions.^{34,35} The electrochemical behavior of the modified electrode showed a good sensitivity to arsenic concentration around maximum permissible according to Argentine legislation.¹⁵ In the following section, the

Table I. Equilibrium swelling percentage and rate constant for the studied hydrogels.

Medium	PNIPAM		PNIPAM-co-50%APTMAC	
	Water	Buffer (pH 9.6)	Water	Buffer (pH 9.6)
% $S_{w_{eq}}$	3185	1824	4472	1494
$k_s \times 10^2 (\text{min}^{-1})$	0.29	0.63	4.22	4.06

electrochemical performance of this electrode in physical contact to the gel is shown.

The electrochemical response of arsenic loaded inside a polymeric hydrogel.—In Figure 7 the CVs of the modified electrode in physical contact with the cationic hydrogel, neutral hydrogel and with the arsenic solution is shown.

As it can be seen in Figure 7 the arsenic oxidation peak current (I_p) in the cationic hydrogel (preloaded in 100 ppb of the arsenic solution-▲) is ca. 8 times higher than the peak current generated by the neutral hydrogel (preloaded in 100 ppb of the arsenic solution-□). Moreover, the electrochemical response for arsenic loaded in the cationic hydrogel was 4 times higher than the peak current obtained

for the same concentration of arsenic in solution. This result would suggest that arsenite anions have been loaded successfully inside of the cationic polymer gel by electrostatic interactions. Barakat et al.⁵² also showed the maximum percentage of sorbed Arsenic at pH 9 according to their the ionization constant value employing cationic hydrogels. Moreover, we have reported that hydrogels with sulfonic ($-\text{SO}_3^-$) groups show large values of partition coefficient of Fe^{+2} into the hydrogel (>500), where the metal interacts by electrostatic interactions with the anionic polymeric networks.³⁻⁵

Moreover, the response obtained in PNIPAM (swelled in a 100 ppb solution of arsenite) is ca. 1.85 times lower than the response measured in solution for the same concentration. Martinez et al.^{3,4} have reported that the diffusion coefficient (D) of a redox complex ($\text{Fe}(\text{Fen})_3^{2+}$) in solution ($D_{\text{solution}} = 4.4 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) is ca. 7.5 times the value inside of this polymeric gel ($D_{\text{gel}} = 5.8 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$). D_{gel} is lower than those in solution due to the larger viscosity of the hydrogel matrix which is in agreement with Stokes-Einstein equation.⁵³ Since the peak current scales up with $D^{1/2}$, the decrease of D accounts for the lower peak current.⁴³ Assuming that the same ratio of diffusion coefficients exists in this gel and the concentration inside and outside of the hydrogel is the same, a ratio of 2.7 should be expected which is close to the observed ratio of 1.85.

To validate the aforementioned approach in cationic co-polymer gel arsenite coefficient diffusion should be determinate. However, the mass transport parameters for arsenite are difficult to determine

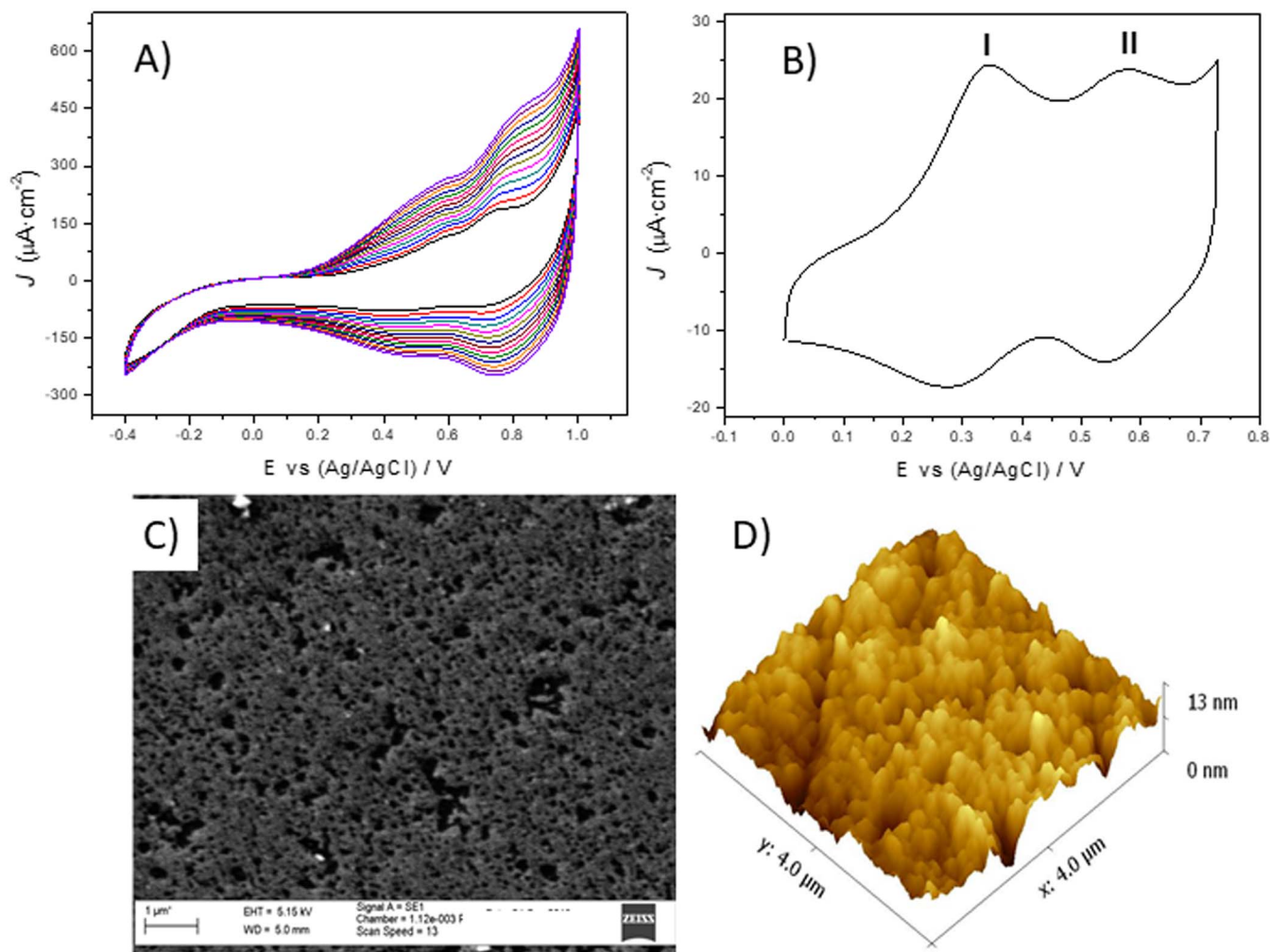


Figure 5. A) Electrodeposition of cobalt oxide from $\text{CH}_3\text{COONa}/\text{CoCl}_2$ solution on GC electrode. Potential window: -0.4 to 1 V. Scan rate $100 \text{ mV} \cdot \text{s}^{-1}$. B) Cyclic Voltammetry of CoOx/CG electrode in a buffer solution pH 9.6. Potential window: 0 to 0.7 V. Scan rate $10 \text{ mV} \cdot \text{s}^{-1}$. C) SEM image and D) AFM image of the CoOx/CG electrode.

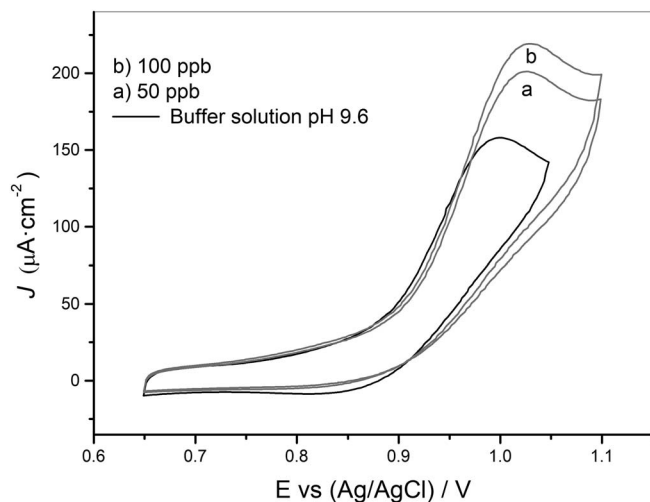


Figure 6. Cyclic voltammograms of the arsenic-free buffer solution pH 9.6, a) 50 ppb arsenic and b) 100 ppb arsenic solutions using CoOx/GC electrode. Potential window: 0.65 to 1.1 V. Scan rate $10 \text{ mV} \cdot \text{s}^{-1}$.

because the electrochemical mechanism involves slow charge transfer and coupled chemical reactions. Therefore, a similar anion (ferri-cyanide) was chosen to determine the diffusion coefficient ratio inside/outside of cationic co-polymer gel by using a glassy carbon electrode as a negative redox probe molecule. It was determined that D_{gel} ($5.9 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$) is almost 300 times lower than in the solution ($1.7 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$). Thus, assuming a similar ratio on the diffusion coefficients for arsenite ions a diminution of 17 times on the current density ratio at the same concentration inside/outside of the cationic co-polymer gel should be expected. However, the peak current measured inside was ca. 4 times larger than that measured in solution. This result would indicate that a selective sorption of analyte clearly overcomes any diffusional effect using the cationic hydrogel.

Moreover, in comparison with the electrochemical response of CoOx/GC in arsenic solution (Figure 6), Figure 7 shows that the peak current inside the gel also increased by increasing arsenic solution. However, the gap between the peak current in absence and 50 ppb arsenic concentration was slightly lower in the cationic polymeric gel than in the arsenic solution. In conclusion, 50 ppb of arsenic could be considered as the threshold limit of arsenic detection for this method

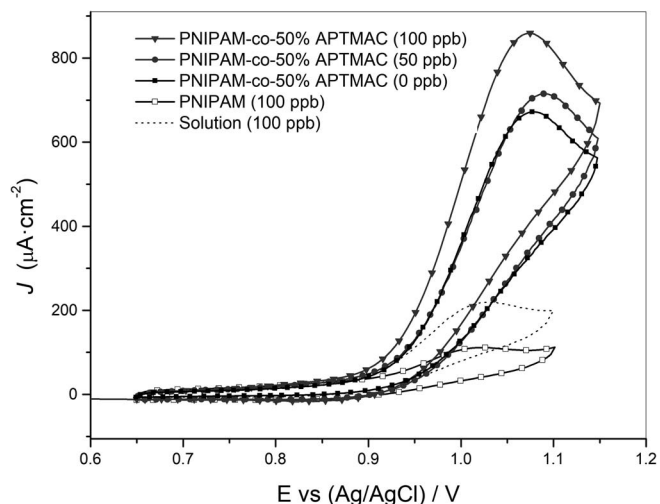


Figure 7. Cyclic voltammograms of the 100 ppb arsenic solution (dotted line); 100 ppb arsenic preloaded in PNIPAM hydrogel (open square (\square)); and of the blank buffer solution (filled square (\blacksquare)); 50 ppb arsenic (filled circle (\bullet)); 100 ppb arsenic (filled triangle (\blacktriangledown)) preloaded in PNIPAM-co-50% APTMAC using CoOx/GC electrode, respectively. Potential window: 0.65 to 1.1 V. Scan rate $10 \text{ mV} \cdot \text{s}^{-1}$. Buffer solution pH 9.6.

and this simple procedure could be used to indicate if the analyzed water satisfies the drinking-water quality.

Measurements in real samples: arsenic sensing in tap water.—

It was proved that the system formed by a CoOx/GC electrode in contact with a cationic hydrogel is able to sensitively detect above 50 ppb of arsenic in synthetic stock samples at pH 9.6. In this section, the electrochemical performance of the proposed method to detect arsenic in tap water samples from different cities of Argentina, where arsenic levels are higher than the accepted threshold limit, is shown.³⁸

Figure 8A shows the CV profiles for an arsenic stock sample at 50 ppb (black line) inside the PNIPAM-co-50% APTMAC gel. Figure 8B shows the CV responses for each tap water sample studied employing a PNIPAM-co-50% APTMAC gel. Comparing the CV responses in both graphics, it is possible to conclude that all the analyzed samples showed arsenic levels above to 50 ppb. Moreover, taken into account the peak current obtained when the cationic gel was preloaded with 100 ppb arsenic stock sample (Figure 7), it is possible to conclude

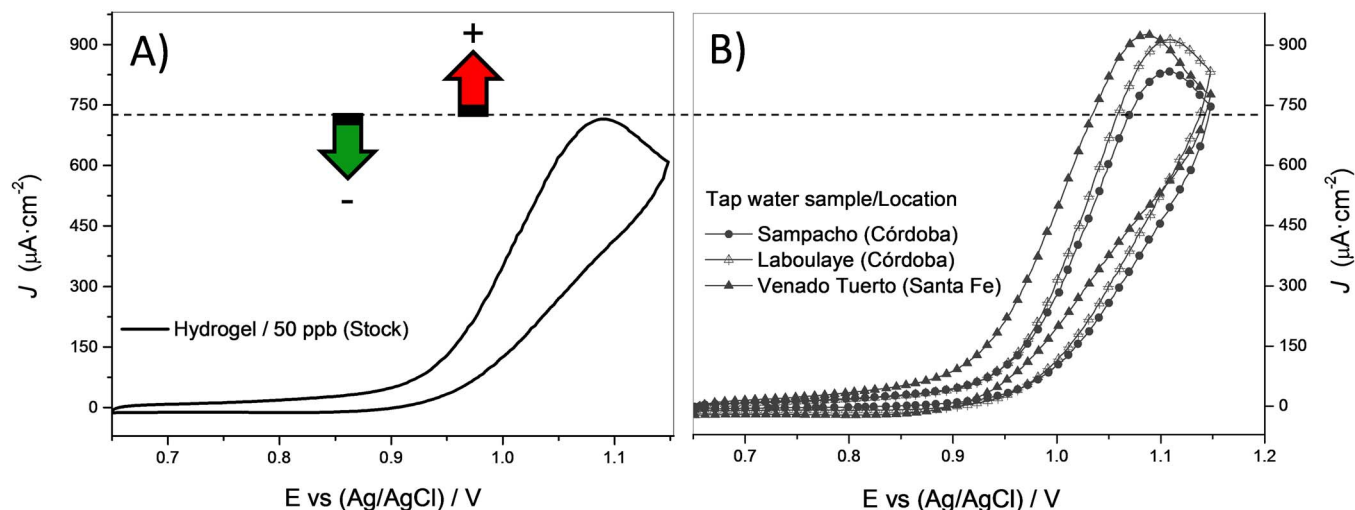


Figure 8. Cyclic voltammograms of the A) 50 ppb arsenic stock solution (black full line), and B) the tap water samples from different cities (see insert) preloaded in PNIPAM-co-50% APTMAC using CoOx/GC electrode. Potential window: 0.65 to 1.1 V. Scan rate $10 \text{ mV} \cdot \text{s}^{-1}$. Buffer solution pH 9.6.

Table II. Arsenic level for the studied water sample.

Tap water samples Location	As(III)*	As (III)**
Sampacho (Córdoba, Argentina)	100 ppb	ca. 100 ppb
Laboulaye (Córdoba, Argentina)	136 ppb ⁵⁴	>100 ppb
Venado Tuerto (Santa Fe, Argentina)	141ppb ⁵⁴	>100 ppb

*Atomic Absorption Spectrometry.

**Method proposed.

that the studied water samples present arsenic concentration close or above to 100 ppb.

The results obtained by using the proposed method are in agreement with those reported before employing other standard detection methods, see Table II.

Conclusions

The performance of the proposed method involving the electrochemical detection of an analyte loaded in a polymeric gel was tested. Based on the results, it is possible to conclude that a useful method for arsenic sensing which combines the arsenite sorption inside a cationic polymeric hydrogel and electrochemical detection by a modified electrode of glassy carbon with cobalt oxide nanoparticles was developed.

The oxidation peak current of arsenic in the cationic hydrogel increases ca. 4 times compared with the measured value at the same arsenic concentration (100 ppb) in solution, showing the potential of the polymeric gel to electrochemically sense ions in water matrices. Also, the method is able to detect above 50 ppb of arsenic in water and allow building a sensor that determines the maximum arsenic level permissible according to Argentine legislation.

The proposed method has proved to be an alternative for routinely and on-field analysis due to its easy to use with a little pre-treatment of the sample. Finally, the electrochemical platform employing a hydrogel soft matrix could be extended to sense other ions by using different polymeric gels and of modified electrodes in complex matrices.

Acknowledgments

D.F. Acevedo, M.M. Bruno, and C.A. Barbero are permanent research staff of CONICET. M.V. Martínez and R. Coneo Rodríguez thank CONICET for a graduate fellowship. The funding of CONICET, CIN, SECYT-UNRC, SPU, and FONCYT are gratefully acknowledged.

ORCID

Mariano M. Bruno  <https://orcid.org/0000-0002-7004-7782>

References

- M. Molina, C. Rivarola, and C. Barbero, *Eur. Polym. J.*, **47**, 1977 (2011).
- M. Barakat and N. Sahiner, *J. Environ. Manage.*, **88**, 955 (2008).
- M. V. Martínez, M. M. Bruno, M. C. Miras, and C. A. Barbero, *Electrochim. Acta*, **219**, 363 (2016).
- M. V. Martínez, R. C. Rodríguez, A. B. Moncada, C. R. Rivarola, M. M. Bruno, M. C. Miras, and C. A. Barbero, *J. Solid State Electrochem.*, **20**, 2951 (2016).
- M. V. Martínez, C. R. Rivarola, M. C. Miras, and C. A. Barbero, *Sens. Actuator B-Chem.*, **241**, 19 (2017).

- W. H. Organization, *Guidelines for Drinking-water Quality, Chemical fact sheets* http://www.who.int/water_sanitation_health/dwq/gdwq0506_12.pdf, accessed 6 nov 2018.
- S. Rahman, K.-H. Kim, S. K. Saha, A. M. Swaraz, and D. K. Paul, *J. Environ. Manage.*, **134**, 175 (2014).
- A. K. Dwivedi, S. Srivastava, S. Dwivedi, and V. Tripathi, *Hydrology: Current Research*, **6**, 4 (2015).
- IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, *World Health Organization, International Agency for Research on Cancer, Some drinking-water disinfectants and contaminants, including arsenic*, IARC (2004).
- S. J. Flora, in *Handbook of arsenic toxicology*, Elsevier (2015).
- S. S. Fariñas, V. A. Casa, C. Vázquez, L. Ferpozzi, G. N. Pucci, and I. M. Cohen, *Sci. Total Environ.*, **309**, 187 (2003).
- R. Nickson, J. McArthur, W. Burgess, K. M. Ahmed, P. Ravenscroft, and M. Rahman, *Nature*, **395**, 338 (1998).
- P. L. Smedley and D. G. Kinniburgh, *Appl. Geochem.*, **17**, 517 (2002).
- B. K. Mandal and K. T. Suzuki, *Talanta*, **58**, 201 (2002).
- “Plan nacional de agua potable y saneamiento”, https://www.argentina.gob.ar/sites/default/files/interior_agua_plan_agua_saneamiento.pdf, accessed 6 nov 2018.
- F. Cubadda, B. P. Jackson, K. L. Cottingham, Y. O. Van Horne, and M. Kurzius-Spencer, *Sci. Total Environ.*, **579**, 1228 (2017).
- J. Luong, E. Majid, and K. Male, *Open Anal Chem J*, **1**, 7 (2007).
- S. Kempahanumakkagari, A. Deep, K.-H. Kim, S. K. Kailasa, and H.-O. Yoon, *Biosens. Bioelectron.*, **95**, 106 (2017).
- Y.-C. Sun, J. Mierzwa, and M.-H. Yang, *Talanta*, **44**, 1379 (1997).
- M. Kotouček, J. Vašicová, and J. Růžička, *Microchimica Acta*, **111**, 55 (1993).
- X. Dai, O. Nekrassova, M. E. Hyde, and R. G. Compton, *Anal. Chem.*, **76**, 5924 (2004).
- M. L. Yola, N. Atar, M. S. Qureshi, Z. Üstündağ, and A. O. Solak, *Sens. Actuator B-Chem.*, **171–172**, 1207 (2012).
- M. L. Yola, T. Eren, H. İlkimen, N. Atar, and C. Yenikaya, *J. Mol. Liq.*, **197**, 58 (2014).
- V. K. Gupta, M. L. Yola, N. Atar, Z. Ustündağ, and A. O. Solak, *Electrochim. Acta*, **112**, 541 (2013).
- V. K. Gupta, M. L. Yola, N. Atar, A. O. Solak, L. Uzun, and Z. Üstündağ, *Electrochim. Acta*, **105**, 149 (2013).
- C. Göde, M. L. Yola, A. Yılmaz, N. Atar, and S. Wang, *J. Colloid Interface Sci.*, **508**, 525 (2017).
- R. T. Kachosangi and R. G. Compton, *Sens. Actuators, B*, **178**, 555 (2013).
- S. Prakash, T. Chakrabarty, A. K. Singh, and V. K. Shahi, *Electrochim. Acta*, **72**, 157 (2012).
- S. Dash and N. Munichandraiah, *Analyst*, **139**, 1789 (2014).
- X. Dai and R. G. Compton, *Electroanalysis*, **17**, 1325 (2005).
- A. Profumo, M. Fagnoni, D. Merli, E. Quartarone, S. Protti, D. Dondi, and A. Albini, *Anal. Chem.*, **78**, 4194 (2006).
- G. Ramesha and S. Sampath, *Sens. Actuator B-Chem.*, **160**, 306 (2011).
- M. Yang, Z. Guo, L.-N. Li, Y.-Y. Huang, J.-H. Liu, Q. Zhou, X. Chen, and X.-J. Huang, *Sens. Actuator B-Chem.*, **231**, 70 (2016).
- A. Salimi, H. Mamkhezri, R. Hallaj, and S. Soltanian, *Sens. Actuator B-Chem.*, **129**, 246 (2008).
- R. Coneo-Rodríguez, A. Baena-Moncada, D. F. Acevedo, G. M. Morales, G. A. Planes, and C. A. Barbero, *J. Solid State Electrochem.*, **22**, 1257 (2018).
- Y. Tian, M.-L. Chen, X.-W. Chen, J.-H. Wang, Y. Hirano, H. Sakamoto, and T. Shirasaki, *J. Anal. At. Spectrom.*, **26**, 133 (2011).
- D. Chen, C. Huang, M. He, and B. Hu, *J. Hazard. Mater.*, **164**, 1146 (2009).
- F. M. Francisca and M. E. Carro Perez, *Environ. Geochem. Health*, **31**, 673 (2009).
- E. O. Kartinen and C. J. Martin, *Desalination*, **103**, 79 (1995).
- I. G. Casella and D. A. Di Fonzo, *Electrochim. Acta*, **56**, 7536 (2011).
- B. Stuart, *Infrared spectroscopy*, Wiley Online Library (2005).
- I. Yudovin-Farber, N. Beyth, E. I. Weiss, and A. J. Domb, *J. Nanopart. Res.*, **12**, 591 (2010).
- A. J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, Wiley New York (1980).
- Z. Zhao, Z. Li, Q. Xia, E. Bajalis, H. Xi, and Y. Lin, *Chem. Eng. J.*, **142**, 263 (2008).
- S. Zhao, *Environ. Sci. Technol.*, **48**, 4212 (2014).
- Y. Zhao, J. Kang, and T. Tan, *Polymer*, **47**, 7702 (2006).
- L. Arens, F. Weißenfeld, C. O. Klein, K. Schlag, and M. Wilhelm, *Advanced Science*, **4**, 1700112 (2017).
- S.-J. Li, J.-M. Du, J. Chen, N.-N. Mao, M.-J. Zhang, and H. Pang, *J. Solid State Electrochem.*, **18**, 1049 (2014).
- H. Heidari and E. Habibi, *Microchimica Acta*, **183**, 2259 (2016).
- S. K. Meher and G. R. Rao, *J. Phys. Chem. C*, **115**, 15646 (2011).
- J. A. Koza, Z. He, A. S. Miller, and J. A. Switzer, *Chem. Mater.*, **24**, 3567 (2012).
- M. A. Barakat and N. Sahiner, *J. Environ. Manage.*, **88**, 955 (2008).
- C. C. Miller, *Proc. R. Soc. Lond. A*, **106**, 724 (1924).
- NutriRed.org, “*Mapa Arsénico Argentina*,” accessed 6 nov 2018.