

The effect of composition of solid silver amalgam electrodes on their electrochemical response

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Abstract The main purpose of this work was to evaluate the effect of the silver to mercury ratio on the voltammetric responses of silver solid amalgam electrodes (AgSAE's). For this, the AgSAE were prepared by mechanical mixing the metals in the following mass ratios of silver to mercury: 30/70, 40/60, 50/50, 60/40, and 70/30. The resulting AgSAE's were physically characterized by energy dispersive X-ray analysis, X-ray diffraction and scanning electron microscopy, confirming the mass percentages of the silver and mercury, the total absence of liquid mercury and a globular structure of all AgSAE's. Furthermore, it was observed that the AgSAE 30/70 contained only one single phase (Ag_2Hg_3), and no metallic silver or mercury oxides. Additionally, the resulting AgSAE's were chemically characterized with respect to the influence of the electrode composition on the reproducibility and electrochemical signals of a hexamine-ruthenium (III) chloride solution by use of electrochemical impedance spectroscopy and cyclic voltammetry. The separation between anodic and cathodic peaks, and consequently, the charge transfer resistance across the electrode/solution interface, and the electroactive area were calculated demonstrating that the 30/70 composition is the best surface for practical applications. Finally, square-wave voltammetry experiments were performed in 4-nitrophenol solution, with a previous optimization of the

experimental and voltammetric parameters. The calculated detection limit shows that the AgSAE 30/70 is suitable for determining any contamination by *p*-nitrophenol, minimizing the toxic residues in case of using liquid mercury electrodes.

Keywords Silver solid amalgam electrode · Amalgam electrode · Mercury waste · *p*-Nitrophenol · Square-wave voltammetry

Introduction

Mercury electrodes have highly reproducible, smooth, and readily renewable surfaces [1]. However, in recent years various attempts have been made to develop new materials for the construction of working electrodes that reduce or avoid the use of liquid mercury, mainly in order to avoid the generation of toxic Hg waste. Further, it is difficult to use mercury electrodes for field analysis and in flowing systems. Finally, mercury electrodes are limited in their application to compounds with signals in the negative potential range [2].

In order to improve the situation, various materials have been proposed as working electrodes. At present, the silver solid amalgam electrode (AgSAE) is one of the most frequently used, because it combines the properties of liquid mercury with some of the properties of silver [3, 4]. The AgSAE presents a solid and homogeneous surface, allowing an easy renewal by mechanical polishing [5–8] and, most importantly, the use of AgSAE's minimizes the risk of environmental contamination with mercury since the amount discarded in each analysis is minimal.

AgSAE's offer a wide range of working potentials, limited only in the positive potential range by the electro-oxidation of mercury, and in the negative range by the

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hydrogen evolution reaction. Both reactions are strongly dependent of the medium used in the voltammetric experiments. The surface of the AgSAE's is chemically stable in the solutions commonly employed as the supporting electrolyte and does not react with air to form oxides on the electrode surfaces. Neither do AgSAE's form intermetallic compounds with other metals present in the analysis medium [9].

The main purpose of this work was to construct and characterize, both chemically and physically, AgSAE's with different ratios of silver to mercury and to investigate the effect on the electrochemical behavior and analytical response, especially with respect to the reduction process of 4-nitrophenol (4-NP). This is a phenolic compound derived from pesticide degradation, car exhausts and industrial wastes, and presents high toxicity for humans and the environment.

Experimental

All voltammetric measurements were carried out using an Autolab model PGSTAT 30 potentiostat from Metrohm-EcoChemie, controlled by a personal computer using GPES software (General Purpose Electrochemical System) version 4.9 and frequency response analyzer software, also from Metrohm-EcoChemie.

In all voltammetric experiments, a conventional cell was used with a three-electrode system, incorporating a Ag/AgCl/Cl⁻ (3.0 mol/l) electrode as reference electrode, a platinum wire as the auxiliary electrode and the AgSAE as the working electrode.

The AgSAE's were manufactured using different mass ratios of silver to liquid mercury (Ag/Hg; *m/m*). For this, a suitable quantity of analytical-grade liquid mercury (purity, 99.99% from Synth) and between 30% and 70% of fine silver powder (particle size, 5–9 μm; purity, 99.9% from Sigma-Aldrich) were vigorously blended. Immediately after blending, the produced paste amalgam was inserted into a Pyrex[®] glass capillary tube with an inner diameter of about 0.30 mm and pressed in for full compaction. After 10 min, the paste amalgams were solidified, and the electric contact was provided by a copper wire affixed with silver adhesive to the paste.

The resulting disks were set aside for 1 day to complete the amalgamation reaction. The resulting solid amalgam disks were polished with a 0.1-μm alumina powder and used in subsequent experiments. The samples of AgSAE's for physical characterization were prepared similarly to the working electrodes.

The morphology and elemental analyses of AgSAE's were evaluated by scanning electron microscopy (SEM)

equipped with energy dispersive X-ray (EDX) detection. The microscope was a LEO Mod. 440 with a SiLi detector and it was run with 63 eV.

The chemical structures of AgSAE's were analyzed by X-ray diffraction (XRD), using a Rigaku diffractometer (Rigaku Corp., Tokyo, Japan) model D-Max 2500 PC with Cu/40 kV/150 mA radiation and a fixed monochromator. A 2θ range from 20.00 to 60.00 was used with step intervals of 0.020° and a photon-counting time of 10 s per step. The XRD data were analyzed with the crystallographic search-match software [10], which is a search-match program, to identify the components of a multi-phase powder diffraction pattern.

The voltammetric characterization was performed using the responses obtained by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of a solution of hexamine-ruthenium (III) chloride [Ru(NH₃)₆Cl₃], (98% purity, from Aldrich) in an electrolyte composed of Sorensen buffer, pH 7.0. CV experiments were carried out by cyclic scanning from 0 to -0.4 V, with potential sweep rates from 0.01 to 0.2 V/s.

The same solution was employed for EIS experiments, where the potentiostatic mode was used, applying -0.23 V for 600 s, which corresponded to the cathodic peak observed for the reduction process of the Ru(NH₃)₆Cl₃. The frequency of the voltage perturbation signal was varied from 0.01 Hz to 100 kHz, using an AC of 10 mV amplitude. The Z-view (Scribner Associates Inc.) software [11] was used to estimate the equivalent circuits for each electrode employed in order to analyze the EIS experiments.

All chemicals were of analytical reagent grade. A 0.1 mol/l Britton–Robinson (BR) buffer was employed as the supporting electrolyte for experiments using 4-NP. The pH was adjusted to the desired value via the addition of appropriate amounts of a 1.0 mol/l NaOH stock solution.

A 1.0 × 10⁻³ mol/l stock solution of 4-NP (98% purity from Merck) was prepared by dissolution of an appropriate quantity in ultra-pure water, which was stored in a dark flask and kept in the refrigerator to avoid degradation.

All measurements were carried out under ambient conditions. The appropriate solutions were transferred into the electrochemical cell, where they were deaerated by bubbling nitrogen. In addition, the electrochemical cell was kept under a nitrogen atmosphere throughout the experiments. Analytical curves were constructed using the experimental and voltammetric parameters previously defined by Garbellini and co-workers [12].

Before each day of experiments or after every interval longer than 1 h, the working electrodes were activated according to a procedure described previously [2, 4, 6, 9] applying -2.20 V from 0 to 600 s in a 0.20 mol/l KCl solution while stirring.

Results and discussion

Physical characterization

The EDX analysis of AgSAE's samples have shown that the metal ratio of the electrodes completely agree to the ratios which have been used to prepare the amalgams. These results indicate that no metal was lost during the preparation and assembling of the electrodes. There was also no oxide formation, similar to previously observations by Fadn [13].

The SEM analysis was used to evaluate the morphology of the AgSAE's constructed by different ratios of mercury to silver. The morphology observed in case of all electrodes is rough and irregular, and by the major magnification possibility it was possible to observe the presence of a crystalline type structure formed by compact and globular crystals. However, when the Hg content increases in the amalgam the size of globules increases and is better defined, as shown in micrographs obtained for the ratio 30/70 with 1,000 and 5,000 times magnifications, respectively (cf. Fig. 1). That increase in formed globules could indicate a higher electroactive area (A). The SEM analysis performed after polishing the electrodes has shown that the morphology was not modified, indicating that the physical crystalline structures of the AgSAE's were not affected by the polishing.

XRD was used to characterize the crystallographic structure of all of the electrodes. Using commercial software, the position of each peak was analyzed and compared to databases of standards for all possible crystalline structures, including all compounds containing oxygen, silver, and mercury. The diffraction lines corresponding to phase Ag_2Hg_3 were detected in all samples, regardless of the Ag/Hg ratios (PDF 11-0067) [10]. However, this phase was predominant only in the sample with the ratio 30/70 (Ag/Hg; *m/m*); in all other samples a mixture of Ag_2Hg_3 , Ag_3Hg_2 , AgHg, and sometimes silver was present.

Furthermore, in the 30/70 (Ag/Hg; *m/m*) sample, no diffraction lines were observed corresponding to oxide formation, indicating that this ratio is suitable for analytical purposes, allowing for the polishing procedure of the electrode surface without interfering with the reproducibility of the responses.

Electrochemical characterization

The AgSAE's made of materials with different Ag/Hg ratios were electrochemically characterized by analysis of the voltammetric responses of a redox couple with the well-known voltammetric system $[\text{Ru}(\text{NH}_3)_6\text{Cl}_3]$, where one can study the separations between the cathodic and anodic

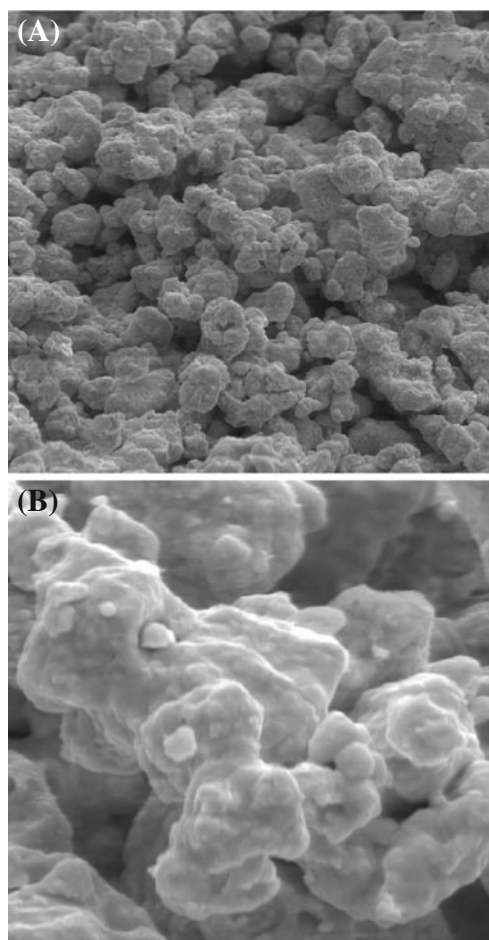


Fig. 1 Scanning electron microscopy images of AgSAE with 30/70 proportions of Ag/Hg (*m/m*), where the bar is 1.0 μm and the magnification employed was $\times 1,000$ (a) and $\times 5,000$ (b)

peaks, and consequently the charge transfer resistance, and also calculate the electroactive area for each electrode. Figure 2 shows the cyclic voltammograms obtained in solutions of 4.39×10^{-3} mol/l $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ using all electrode compositions. The measured separations between the cathodic and anodic peak, i.e., the peak-to-peak separation (ΔE_p) calculated for each electrode employed, are shown in Table 1.

The analysis of the ΔE_p values suggests that a higher mercury content of the electrodes leads to smaller separations between the anodic and cathodic peaks (ΔE_p), i.e., shifts the one-electron-transfer reaction towards higher reversibility. Those values demonstrate the efficiency in the electron-transfer mechanism across the electrode/solution interface in the electrodes, indicating that the 30/70 composition allows the lower resistance for a charge transfer, and consequently is more adequate to analytical applications.

For all electrodes, the cathodic peak for $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ exhibited a linear relationships with the square-root of the

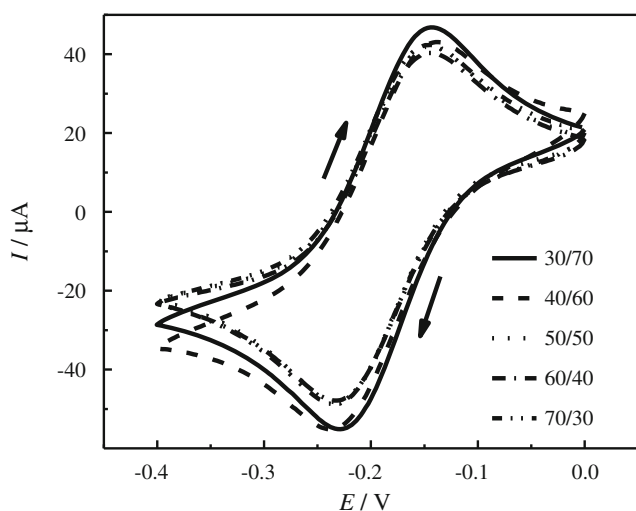


Fig. 2 Cyclic voltammograms for 4.39×10^{-3} mol/l of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in Sorensen buffer, pH 7.0 on the AgSAE constructed using different mass percentages of silver/mercury (m/m). All voltammograms were recorded at 100 mV/s

scan rates, which is typical of a planar diffusion-controlled redox processes. Using the Randles–Sevcik equation, it was possible to determine the electroactive areas for each electrode, as shown in Table 1, using the following:

$$I_p = (2.69 \times 10^5) n^3/2 AC_r^* D_r^{1/2} \nu^{1/2} \quad (1)$$

where I_p is the peak current, n is the number of total electrons involved in the reaction ($n=1$), D_r is the diffusion coefficient of the $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in the medium employed (5.5×10^{-6} cm²/s), C_r is the concentration of the $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (4.39×10^{-3} mol/l), and ν is the potential scan rate (from 0.01 to 0.2 V/s) [14, 15].

Since all of the electrodes had the same geometric area (7.06×10^{-2} cm²), the deviation between geometric surface area and the electrochemically determined area is very small and is due to, probably changing mechanical properties.

Experiments of the EIS were performed for studying the interfacial properties of the AgSAE's with different compositions, by the impedance profile of the system, using the

same solution as was used for CV. The impedance spectra in Nyquist plots exhibited the ideal profile of a purely diffusion-controlled reaction, with a linear correlation of real imaginary and impedances (Z_i and Z_r , respectively) at lower frequency region, which is the impedance corresponding to the diffusion-controlled process. In the Nyquist plot, impedance appears as an almost linear line, with a slope close to one, as shown in Fig. 3.

EIS experiments were also performed using a 4.02×10^{-2} mol/l 4-NP solution in BR buffer, pH 4.0 to evaluate the changes in the interface electrode/solution for an adsorptive process. An AC value of 10 mV was used over a frequency range from 0.01 to 10 kHz, with the potentials operated at -0.56 V.

The Nyquist impedance responses of all AgSAE's showed a semicircle with a high-frequency intercept to an ionic resistance of the solution, and a low-frequency intercept equal to the sum of the ionic resistance and the electron-transfer resistance of the electron.

Considering the high-frequency range, all electrodes presented similar values in its intercept, related to the ionic resistance solution. However, in the low-frequency range each electrode presented a value related to electron-transfer resistance process, followed by a straight line, as observed in Fig. 4.

Using the model based on a Randles equivalent circuit, one can extract the above resistances and capacitances from an EIS experiment conducted on AgSAE's with different compositions. This circuit uses an element related to the resistance of the solution (R_1), an element related to the electron-transfer resistance (R_2) and a constant phase element to compensate for the non-ideal capacitive responses of the interface [16].

The quality of fitting to the equivalent circuit was evaluated by the error values, and the obtained fit values are given in Table 1, showing that the 30/70 (Ag/Hg, m/m) AgSAE has the lowest resistance of the electron-transfer and, therefore, better analytical applicability. The electrodes with the greater electroactive area corresponded to the greater values of CPE, which is related to the capacitance of the electrode.

Table 1 Electroactive areas and separations between cathodic and anodic peaks (ΔE_p) calculated from cyclic voltammetry experiments and element parameters obtained from fitting the equivalent circuit to

the electrochemical impedance spectroscopy measurements on AgSAEs constructed with different mass percentages of silver/mercury (m/m)

Electrode (Ag/Hg, m/m)	Electroactive area (cm ²)	ΔE_p (mV)	R_1 (Ω)	R_2 (k Ω)	CPE1 ($\mu\text{F}/\text{cm}^2$)
30/70	6.57×10^{-2}	69	100.20 ± 0.95	3.90 ± 0.03	5.25 ± 0.10
40/60	5.86×10^{-2}	73	100.65 ± 2.23	4.13 ± 0.10	4.79 ± 0.35
50/50	5.50×10^{-2}	76	99.59 ± 1.12	4.25 ± 0.03	1.88 ± 0.04
60/40	5.48×10^{-2}	78	101.40 ± 1.22	4.84 ± 0.03	1.16 ± 0.02
70/30	5.38×10^{-2}	88	99.89 ± 1.20	5.00 ± 0.03	1.09 ± 0.02

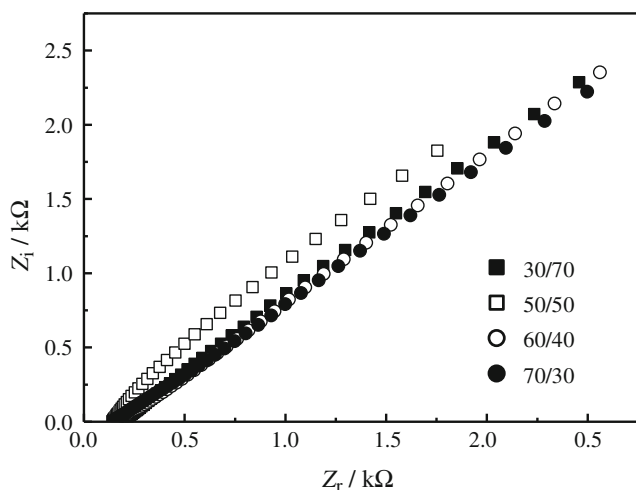


Fig. 3 EIS measurements (Nyquist plots) using different mass percentages of silver and mercury (*m/m*) of 3.9×10^{-3} mol/l of Ru $(\text{NH}_3)_6\text{Cl}_3$ in Sorensen buffer, pH 7.0, with an amplitude sine wave of ± 0.01 V, frequency range from 0.01 Hz to 10 kHz, and the potentials operated at -0.23 V

Electrochemical activation process

The influence of the electrochemical activation process on the analytical responses was evaluated by square-wave voltammetry (SWV) and EIS experiments in a 4-NP solution and BR buffer, pH 7.0. The responses were obtained before and after the activation process. The same equivalent circuit employed in the voltammetric characterization of AgSAE was used to evaluate the responses for the resistance of the charge transfer, before and after the activation steps.

The responses obtained by SWV and EIS (shown in Fig. 5) showed that the electrochemical activation steps of

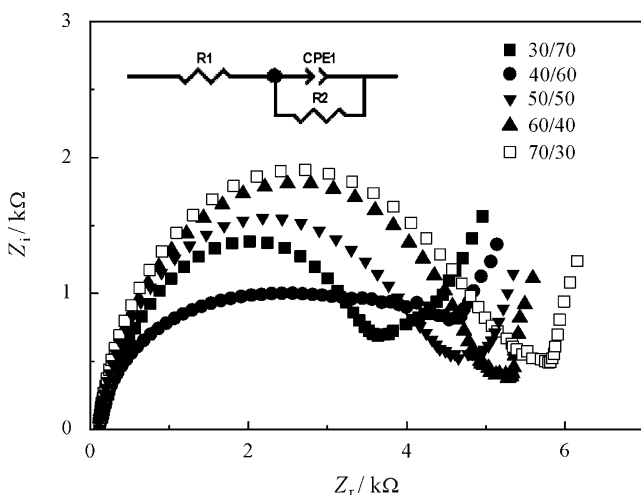


Fig. 4 EIS measurements (Nyquist plots) using different mass percentages of silver and mercury (*m/m*) of 4.02×10^{-2} mol/l of 4-NP solution in BR buffer, pH 4.0 with an amplitude sine wave of ± 0.01 V, frequency range from 0.01 Hz to 10 kHz, and the potentials operated at -0.56 V

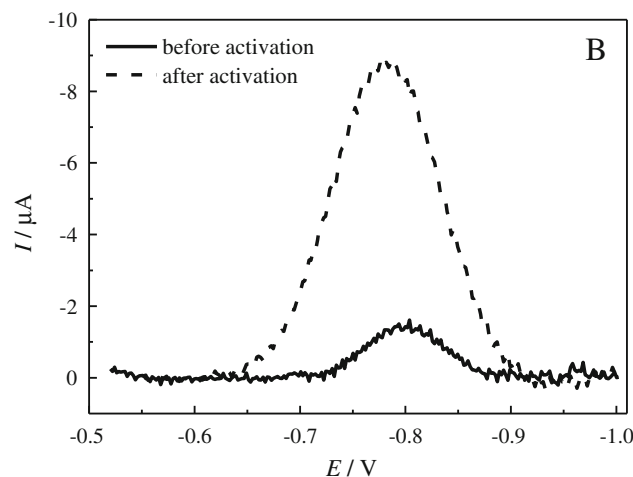
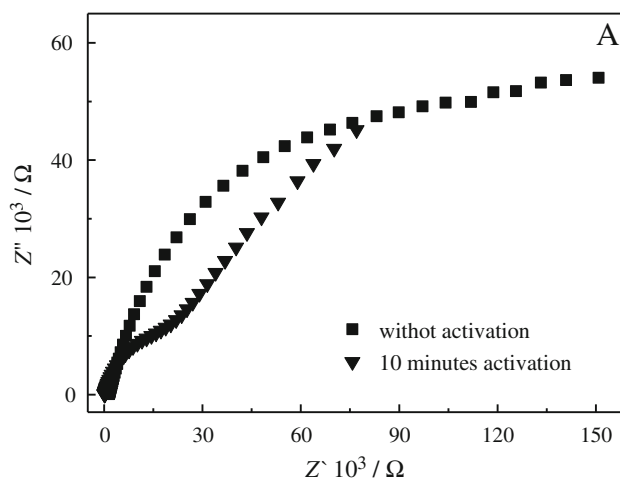


Fig. 5 a EIS measurements (Nyquist plots) for 9.28×10^{-5} mol/l of 4-NP solution in BR buffer, pH 7.0 using a 30/70 (*m/m*) AgSAE with an amplitude sine wave of ± 0.01 V, frequency range from 0.01 Hz to 10 kHz, and the potentials operated at -0.56 V. **b** SWV results for 9.27×10^{-5} mol/l of 4-NP solution in BR buffer, pH 7.0, before and after the electrochemical activation steps, by applying -2.2 V for 5 min and using $f=100$ s $^{-1}$, $a=50$ mV and $\Delta E_s=2$ mV

the electrode surface promote a 100-fold reduction in the resistance to charge transfer and a consequent tenfold increase in the analytical responses, thus constituting a simple, fast, and reliable procedure that improves the analytical sensitivity and also enables the fast and reproducible refreshing of the electrode surface.

A series of SWV experiments were conducted in the same 4-NP solution using SWV to evaluate the number of experiments that can be performed without needing to perform the electrochemical activation process on the electrode surface. The peak current diminished by nearly 8.0% within the first ten experiments. After this, the peak current remained practically constant, indicating that a great number of experiments can be performed without electrochemical activation.

The same SWV experiments were then performed with the electrochemical activation process in the same working

solution. The results of these trials showed that the application of -2.2 V for 30 s is sufficient to remove all adsorbed 4-NP from the electrode surfaces, thereby obtaining a reproducibility of around 2% in the analytical responses, similar to previously observed by other researches [17, 18].

Analytical curves for 4-NP determination on AgSAE 30/70 (Ag/Hg, *m/m*)

After the physical and chemical characterization of the AgSAE's of different composition and the study of the influence of the electrochemical activation process on the analytical responses of the 4-NP reduction process, analytical curves were constructed using SWV experiments for 4-NP in a 0.1 mol/l BR buffer solution, pH 7.0, on the 30/70 (Ag/Hg, *m/m*) AgSAE.

Aliquots from the stock 4-NP solution were consecutively added to the electrochemical cell containing 10 ml of the electrolyte, using the parameters optimized by Garbellini and co-workers [12]: frequency of pulse potential application (f) of 100 s^{-1} , amplitude of pulse potential (a) of 50 mV, and scan increment (ΔE_s) of 2 mV.

The SWV responses were recorded for a concentration range between 5.07×10^{-7} and 4.86×10^{-6} mol/l, where the responses obtained exhibited a linear relationships between the peak currents and concentrations added. The linearity between the peak currents and concentration of 4-NP using the 30/70 (Ag/Hg, *m/m*) AgSAE is described by:

$$I_p(\text{A}) = -6.804 \times 10^{-7} + 0.997C(\text{mol/l}) \quad (2)$$

where I_p is the peak current in amperes (A), and C is the molar concentration of 4-NP in the electrochemical cell.

Using the obtained slope of the analytical curve and the IUPAC definition, the detection and quantification limits could be determined from the following equations:

$$\text{DL} = \frac{3S_b}{s} \quad (3)$$

$$\text{QL} = \frac{10S_b}{s} \quad (4)$$

where S_b is the standard deviation of the arithmetic mean for 10 voltammograms of the blank solution ($S_b = 1.72 \times 10^{-8}$ A mol/l), and s is the slope of the analytical curve [19, 20].

The calculated values of DL and QL were, respectively, 5.20×10^{-8} (7.22 $\mu\text{g/l}$) and 1.73×10^{-7} (24.66 $\mu\text{g/l}$) mol/l. These values are lower than the maximum value (30 $\mu\text{g/l}$) established by the local environmental council for nitropesticides in natural water samples [21].

The DL and QL determined in this work are very close to the values previously obtained using traditional mercury electrodes or modified electrode surfaces [22, 23], indicating

that the AgSAE is a suitable alternative for the electrochemical determination of 4-NP and that this procedure can be successfully employed for the analytical determination of 4-NP.

The precision and accuracy of the procedure using the 30/70 (Ag/Hg, *m/m*) AgSAE for the analytical determination of 4-NP were evaluated by reproducibility and repeatability experiments. The reproducibility of the experiments was determined through five different measurements in the same solution containing 1.02×10^{-6} mol/l 4-NP and 0.10 mol/l BR buffer (pH 7.0), and a variation coefficient value of 2.4% was calculated. The repeatability was also determined by measurements performed in 10 different solutions that contained the same composition as before, and a variation coefficient of 1.95% was obtained. These results are highly indicative that the use of AgSAE 30/70 (Ag/Hg, *m/m*) allows for excellent precision and accuracy in the analytical determination of 4-NP.

Conclusions

The results presented here show that the preparation of AgSAE's is simple, quick, and easy, allowing the preparation of AgSAE's with different ratios of silver to mercury. The described preparation procedure is cost effective and minimizes any environmental contamination with mercury since the entire amount of liquid mercury is completely bonded in the solid amalgam.

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