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FERNANDA CRISTINA DE OLIVEIRA LOPES MARTINS

DENTAL AMALGAM ELECTRODE AS VOLTAMMETRIC SENSOR TO TRIAZINE-BASED PESTICIDES DETERMINATION: APPLICATION IN NATURAL WATER SAMPLES

PATOS DE MINAS – MG

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Orientadora: Profa. Dra. Djenaine de Souza

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Dental amalgam electrode as voltammetric detection of triazine-based: **application in natural water samples**

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Graphical Abstract

Highlights

•   Dental amalgam electrode followed procedures of environmentally friendly guidelines.

•   Dental amalgam electrode had chemical composition and physical structure evaluated.

•   Experimental and voltammetric parameters were optimized by square wave voltammetry.

•   This procedure was used to triazines pesticides detection in natural water samples.

Dental amalgam electrode as voltammetric sensor for triazine-based determinations: application in natural water samples

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Abstract

This paper describes the use of a dental amalgam electrode (DAE) allied to square wave voltammetry (SWV) in the analytical determination of the triazine-based pesticides ametryn (AM), atrazine (AT) and simazine (SI) in natural waters. Experimental and voltammetric parameters were optimized as Brinton-Robinson buffer at pH 2.5, with pulse frequency of 100 s^{-1}, pulse amplitude of 50 mV and scan increment of -2 mV, where the triazines presented well-defined irreversible voltammetric peaks, at -1.05 V, -0.97 V and -0.99 V for AM, AT and SI respectively. For AM and SI was observed a redox reaction controlled by diffusion rate and for AT a reaction controlled by adsorption kinetic. Besides, in AM occurred the reduction of bond carbon-SCH_3 and in AT and SI the reduction of bond carbon-chloride. Analytical curves were constructed, and the voltammetric signals were directly proportional to concentration, and to all triazines, the detection limits were lower than the maximum of residues permitted in natural water by Brazilian Environmental Agency, 100 $\mu g\ L^{-1}$ (100 ppb) and around the obtained using traditional techniques and other electrodic surfaces. The recovery percentages, in pure electrolyte and natural waters, were around 100%, demonstrating that the methodology proposed is suitable for determining any contamination by AM, AT and SI natural waters samples.

1. Introduction

Chemical compounds that act as herbicides, are largely employed in agricultural practice to weed control and eliminate diverse pests types. Its use can minimize of the agricultural work, reduce the cost of production, decrease topsoil erosion, increase of crop yields and consequently the production profits [1]. Among herbicides, the triazines are the chemical class most widely employed in the diverse agricultural productions due to it high efficiency. In Brazil, the ametryn (2-ethylamino-4-isopropylamino-6-methylthio-s-triazine), atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and simazine (2-chloro-4,6-bis(ethylamino)-s-triazine), chemical structures shown in insert in the Fig. 1, are mainly used in the production the corn, sorghum and surge cane [2, 3].

Ametryn (AM), atrazine (AT) and simazine (SI) present moderate soil sorption resulting in the natural water contamination. In the last years, researches shown the accumulative effects on body human, which promote alterations in the metabolism, produce reactions undesirable, and consequently, alteration in hormone functions, development of some cancers types and teratogenic effects [4]. Considering the natural waters, these substances have a maximum limit permitted in the United States and European Union of 3.0 μg L^{-1} [5] and 0.1 μg L^{-1} [6], respectively, it's already in Brazil are permitted 50 μg L^{-1} to AM, AT and SI [3, 7, 8]. So, due to undesirable effects in the environment and human health, herewith is necessary the determination from them in natural waters.

Some reports have demonstrated the use of chromatographic, electroanalytical and spectroscopic techniques to identify and quantify triazines in natural water samples [9 - 13]. Chromatographic techniques has predominance due to its applicability in complex samples and suitable analytical parameters, however, the cost of acquisition and maintenance of the instrumentation is expensive. Nonetheless, the use of electroanalytical techniques promotes an abridgement in the sample preparation steps, provide suitable sensitivity and robustness, present low cost and facility operational [14].

Among the electroanalytical techniques, the square wave voltammetry (SWV) is the most largely employed in the determination of different triazines, including AM, AT and SI [8, 13, 15]. The SWV responses can be used to obtain detailed information regarding the electrochemical behaviour of triazines in environmental interesting samples and mainly its analytical determination in natural waters, owing to certain convenient

analytical features, which include the high sensitivity, accuracy, precision, large linear dynamic range and simplicity in experimental procedure [16].

Moreover, the SWV responses are powerfully related to adequate choices of the working electrode material, due owing the redox reactions happen in the interface electrode/electrolyte. To triazines analysis, the hanging mercury drop electrode (HMDE) is quite employed in reason of its complete renovation surface and excellent reproducibility. Nonetheless, the production of toxic waste provoked the prohibition of the HMDE's use in the all world, and therefore encouraged the researches by new materials with similar properties theirs to traditional mercury electrodes.

Among them, solid amalgam electrode has been are an excellent alternative in the determination of electrochemically compounds reducible, including triazines [17]. These electrodes can be prepared mixing a specific ratio between mercury and other metals, such as copper, silver, gold, iridium, bismuth, among others [18 - 20]. The use of dental amalgam electrodes (DAE) also has been reported as a suitable alternative material in substitution of the HMDE due to its construction procedure is very simple and well established in dental clinical practice. Furthermore, DAE contain only silver and mercury chemically bound as a stable Ag_2Hg_3 alloy, without free liquid mercury, hence is considerate as nontoxic electrode, and its follow the guidelines of the green analytical chemistry [20 - 22].

Therefore, the main goal of this work was the construction, characterization and application of DAE coupled to SWV technique in the electrochemical behaviour study and development of electroanalytical procedure to AM, AT and SI determination in natural water samples.

2. Experimental

2.1 Instrumentation and reagents

The voltammetric experiments were performed using a potentiostat/galvanostat model PGSTAT 101 plus NOVA software version 2.1.2, both from Metrohm-Eco Chemie. All solutions employed were prepared using purified water by a system of the reverse osmosis model OS20 LX from Gehaka. The pH adjustment of the solutions were made in a pHmeter from Tecnopon, model mPA 210, equipped with a 3.00 mol L^{-1} Ag/AgCl/Cl$^-$

glass combined electrode. The mass measurements were achieved in an analytical balance with precision of $\pm$ 0.0001g, from Bel Engineering model M214A.

The physical characterization of the DAE was realized by morphology and elemental analyses using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) techniques, respectively, performed at a scanning electron microscope LEO model 440 coupled to SiLi detector and 63 eV. The alloy produced in the DAE preparation was examined by X-ray Diffraction (XRD), employing a Rigaku diffractometer (Rigaku Corp.,Tokyo, Japan) model D-Max 2500 PC with Cu/40kV/150mA radiation and a fixed monochromator, which a 2θ range from 20.00 to 60.00 was used with step intervals of 0.020 deg and a photon-counting time of 10 s per step. The match program Crystallographic Search-Match [23] was used to identify the components of final DAE.

All chemicals were of analytical-reagent grade. AM (95%), AT (97%) and SI (95%) were obtained from Ouro Fino Agricultural Company, from Minas Gerais, Brazil, and used without purifications steps. 1.00×10^{-4} mol L^{-1} stock solutions of herbicides were daily and individually prepared using pure acetonitrile as solvent, stored in a dark flask and kept in a refrigerator to prevent degradation. All material employed in the voltammetric experiments were preliminary washed with neutral detergent, commercial alcohol 96°GL and pure water for removal of organic wastes.

2.2 Electrochemical cell

A glass conventional cell with a Teflon® cap, containing three electrodes and supporting electrolyte was used in all voltammetric experiments. The homemade DAE, a platinum wire and a 3.00 mol L^{-1} Ag/AgCl/Cl$^-$ electrode were used as working, auxiliary and reference electrodes, respectively. The DAE, previously described by De Souza et al. [20], was prepared according to procedure employed in dental clinics, in which a suitable quantity of analytical grade liquid mercury and fine silver powder (particle size 5-9 μm, purity 99.90%, Sigma-Aldrich), were vigorously blended and inserted into a glass capillary tube with an inner diameter of about 0.30 mm and pressed for full compaction. After this, was formed an alloy like used in dental amalgams, and an electric contact was provided by a copper wire affixed with conductive glue silver. The resulting solid amalgam discs presented a geometric area of 0.071 mm^2 and was polished with ultra-fine sandpaper, washed with water and used in all voltammetric experiments.

Before the voltammetric experiments, the DAE surface was activated by electrochemical procedure previously described, that consisted in the application of the -2.20 V during 600 s, in an electrochemical cell containing 0.20 mol L^{-1} of KCl solution, under constant stirring. This activation procedure was repeated every time or in each new series of experiments with a specify triazine, or after longer breaks one-hour in the voltammetric experiments. Prior to each potential scan, in the electrolyte containing the triazine under study, the surface was renovated by application of the -2.20 V over 30 s, with stirring the solution, previously deoxygenated by bubbling N_2 [20] (White Martins), promoting a decrease in the charge transfer resistance and removal of the adsorbed products of the DAE surface.

2.2 Experimental and voltammetric optimization

Initially were evaluated AM, AT and SI voltammetric responses in the middle of oxalic and Britton-Robinson (BR) buffer, sodium sulphate and sodium perchlorate, which served as supporting electrolyte in pH intervals from 0.5 to 5.0, depending on the electrolyte tested. For this, 10 mL of each supporting electrolyte plus $1.00x10^{-5}$ mol L^{-1} of each triazine standard solutions were transferred into the electrochemical cell and SWV experiments were performed from 0.00 V to -1.20 V, at 25 ± 1 °C, using pulse amplitude (*a*) of the 50 mV, pulse potential frequency (*f*) of 100 s^{-1} and scan potential increment (ΔE_s) of - 2 mV.

After the selection of supporting electrolyte with its adequate pH values, the voltammetric parameters (*f*, *a* and ΔE_s) also were individually evaluates, considering the intensity of peak current (I_p), peak potential (E_p) values and the variation in the half-peak width ($\Delta E_{p1/2}$), which were responsible by sensitivity and selectivity in the analyses.

2.3 Analytical parameters

Behind the experimental and voltammetric optimization, analytical curves were performed using standard addition method, followed by calculous of the detection (LD) and quantification limits (LQ), according to guidelines of IUPAC, where were used the standard deviation of the mean current (S_b) measured at the reduction potentials of each triazine, considering 10 voltammograms of the blank solution in pure electrolytes, jointly with the slope of the straight line of the each analytical curves (s) [24, 25].

The methodology´s accuracy were attest using recovery curves performed in supporting electrolyte and using the standard addition method, considering experiments realized in triplicate, for each triazine. The recovery efficiencies (%R) were calculated considering the ratio between the value of the concentration obtained by extrapolating the recovery curves from the corresponding spiked electrolyte and the concentration previously added [24, 25].

The precision of methodology to AM, AT and SI determinations under DAE were calculated considering the repeatability (*intraday* precision) and reproducibility (*interday* precision) experiments, respectively. Repeatability experiments were accomplished using ten voltammetric analyses, in the same day and in same triazine solution. Reproducibility experiments were accomplished using five voltammetric analysis, in different days and different solutions, considering each triazines. Relative standard deviations (RSD) for repeatability and reproducibility were calculated from standard deviation of the mean current values obtained and the mean peak current values [24,25].

2.4 Application of the proposed methodology

To evaluate to the applicability of the proposed methodology, interfering effects were studied in water sample collected from distinct three points of the Paranaíba River, located at Patos de Minas city, Minas Gerais state, Brazil. These samples were characterized by different organic matter contents, measured Biochemical Oxygen Demand (BOD) [26]. Sample 1 (-18.6554°; -46.5128°) was collected in area located near agricultural plantations of corn, sorghum and soybean, without urban and industrial pollution significant. Sample 2 (-18.6024°;-46.5405°) was collected near of urban area, where the level of pollution by industrial and urban activities is high. Sample 3 (-18.4983°;-46.5603°) was collected in a region after the river traverse all the city, and with the contribution of the higher organic matter contents originating from agricultural, urban and industrial residues.

All samples were used without no pre-treatment steps or/and clean up, except by simple filtration in order to remove all solid particulate components. Posteriorly, 1.0 mL of each sample was added into electrochemical cell containing 9.0 mL of supporting electrolyte and analytical curves were built like described above, considering supporting electrolyte, and LD and LQ were calculated in each sample and for each triazine. After this, recovery curves also were built in these natural water samples, considering a

previously artificial contamination by 2.00×10^{-6} mol L^{-1} of each triazine, separately, to observe the influence of components of each sample in the signal current and this way, verify the robustness of the proposed procedure.

3. Results and discussion

3.1. Physical characterization of DAE

DAE was characterized physically to evaluate its chemical composition, the morphology and the alloy type formed during the amalgamation process, using EDX, SEM and XDR, respectively. The results observed by EDX analysis shown that the metal ratio of the DAE was 45.01% and 54.99% for silver and mercury (Ag/Hg; m/m), respectively, these values are around to the ratios that initially were weighted in the preparation steps, 50% for each element and the difference observed can be related to some loss during the assembling process. Additionally, no oxide formation or the presence of silver and mercury free were observed, in agreement with previously published work [21, 20].

The SEM analysis using 1000 times of magnification shown that the DAE had a morphology rough and irregular, and with 5000 times magnifications was observed the presence of a crystalline type structure formed by compact and globular crystals, as shown in the *Supplementary data*. Additionally, was observed that the DAE morphology was not modified after polishing the electrodes indicating that it's the physical crystalline structures was not affected by the mechanical polishing.

XRD analysis allied to use of a commercial software [23], containing databases of standards for all possible crystalline structures of all compounds containing oxygen, silver and mercury, permitted determine the crystallographic structure of DAE. So, the diffraction lines observed were corresponding to phases Ag_2Hg_3 and Ag_3Hg_2, no diffraction lines were observed corresponding to oxide formation and silver or mercury free, indicating an environmentally friendly electrode, according to recommended by Green Analytical Chemistry guidelines [27].

3.2. Experimental optimization

Preliminary experiments concerning adequate choice of supporting electrolyte were performed in BR and oxalic buffer, sodium sulphate and sodium perchlorate, with pH values from 0.5 to 5.0, according to electrolyte tested. For this, scan potentials were performed from 0.0 V to -1.2 V using SWV experiments with $f = 100$ s^{-1}, $a = 50$ mV and

ΔE_s = -2 mV. In all SWV experiments was observed the conditions were the peak current (I_p), peak potential (E_p) and self-height width variation ($\Delta E_{p1/2}$) values produce a suitable sensitivity and selectivity. So, these preliminary experiments, demonstrated that the better analytical signals for AM, AT and SI were obtained in the BR buffer, and SWV experiments obtained in the pH intervals from 2.0 a 5.0 are shown in Fig. 1, with the respective relationships between I_p and E_p with pH values for each triazine.

FIGURE 1

As demonstrated in Fig 1, to AM appeared a well-defined peak reduction, in which the E_p shifts towards more negative values as the pH increases and the I_p had the maximum value at pH 2.5, bellow the value of pK_a reported in the literature [2], indicating that in pH 2.5 occurred the predominance of the reduction reaction of the AM in its protonated form. Moreover, the relationship between E_p and pH values, exhibited in Equation 1, indicated that the electrochemical reduction process of involved the same number of protons and electrons, like observed using copper solid amalgam electrode (CuSAE) and HMDE [13, 15]:

$$E_p(V) = -0.760 + 0.079\text{pH} \hspace{4cm} \text{Equation 1}$$

To AT was observed the presence a well-defined voltammetric peak only in pH 2.5 and 3.0, which correspond to values above the pK_a reported in the literature [2] (pH > pK_a), typical of the redox reaction involving the formation of very reactive chemical species [28]. Furthermore, no linear relationship was observed to E_p with pH increase, indicating that the use of DAE produced voltammetric responses considerable different of those obtained under CuSAE and HMDE. Even so, the signals observed presented suitable characteristics to electroanalytical procedures. In the SI signals, was observed a well-defined peak voltammetric peak in all pH values, however the maximum of I_p occurred at pH 2.0 and 3.5, that presented a considerable increase in the $\Delta E_{p1/2}$ and were above of the pK_a reported (pH > pK_a), owing, that like AT, probably occurs the formation of very reactive chemical species, followed by protonation steps. Additionally, nonlinear relationships between I_p and E_p with pH values were observed, indicating this way, that protonation is not the determining steps in the redox reactions kinetic [29].

Considering all triazines signals presented in Fig. 1, with its respective structural formulas jointly electrochemical basic aspects of organic compounds reduction process [30], is possible to estimate that a possible redox reaction under DAE occurs at thiol group

(-SCH$_3$) in AM, that present an intense interaction with the silver present in the DAE composition, which promoted the best voltammetric signals. To AT and SI, the redox reactions probably involves the chloride reaction as substituent in triazinic ring, and the differences observed are related to differences in the molecule symmetry, as shown in the Fig. 1 inserts. Additionally, in all posteriorly experiments, the pH 2.5 was chosen due to present, in all triazines, well-defined voltammetric peaks, mainly considering $\Delta E_{p1/2}$ and interval of the E_p, minimizing the energy involved in the electron transfer and possible interferences effects in complex samples, such as natural waters.

Analytical experiments were performed in order to obtain a suitable reproducibility in the voltammetric signals for all triazines, which consisted of the polishing of the DAE, agitation of the solution and electrochemical renovation of the DAE between each experiment. This way, was observed that the polishing promoted considerable alterations in electrode surface, resulting in alterations of the intensities of signal for each triazine, and the agitation of the solution no promoted a complete clean of the DAE, mainly AT. Finally, was observed that the electrochemical renovation by application of -2.2 V by 30 s promoted a complete renovation in the DAE surface, resulting a suitable repeatability and reproducibility in the voltammetric signals, as shown in *Supplementary data,* with E_p values in -1.05 V, -0.97 V and -0.99 V for AM, AT and SI, respectively.

3.3. Voltammetric parameters optimization

The voltammetric parameters were optimized for 1.00x10^{-5} mol L^{-1} of each triazine in BR buffer (pH 2.5), and the relationships between I_p and E_p with *a,* ΔE_s and *f* parameters were individually evaluated in the range from 5 mV to 50 mV, from -2 mV to -10 mV and from 10 s^{-1} to 200 s^{-1}, respectively. The resulting voltammograms of the *f* values variation plus the relationships between I_p and *f* are shown in the Fig. 2, for AM, AT and SI, and the analysis of these voltammograms provides a good criterion for diagnosis and were used to indicate process of adsorption or reaction in solution, reversibility or irreversibility of the electrochemical process, besides the optimization of the best values to obtain sensitivity and selectivity in the proposed procedures [16, 31].

FIGURE 2

Considering the signals shown in Fig. 2, can be observed that for all triazines, occurred a proportionally increase in the I_p values until 100 s^{-1} and a dislodgment in the E_p

values to less negative direction, indicating lower energy associated to electrons transfer at higher scan rate, typical of fast redox reaction [16].

Furthermore, can be observed in the inserts of each voltammograms set, that to AM and SI a linear relationship was observed between the I_p and the f square root, typical of the redox reaction controlled by diffusion rate of the AM and SI from the bulk solution to DAE interface. Moreover, this behavior is typical of redox reactions involving reactant adsorption, where to AM occurred an interaction between the -SCH$_3$ group from AM structure with the silver present in the DAE compositions. Considering the AT, the relationship between f and I_p values presented a linear dependence, typical of redox reactions controlled by adsorption kinetic, followed by product adsorption, which was confirmed by intense peak enlargement. These conclusions originated from considerations of the theoretical model proposed by Lovric et al. for SWV experiments and previously works published to triazines-based pesticides analysis using HMDE [8, 13, 15, 16].

Farther, as shown in Fig. 2, the increase in the f values promoted a shift towards less negative values in the E_p, which varied linearly with the logarithmic value of the frequency according to the following expression, known as Lovric's Equation [20]:

$$\frac{\Delta E_p}{\Delta \log(f)} = \frac{-2.3RT}{\alpha nF}$$ Equation 2

where R is the gas constant; T is the temperature; α is the electron transfer coefficient; n is the number of electrons; and F is the Faraday constant. From equation 2, a plot of ΔE_p *vs* Δlog (f) gives straight line curve defined by Equations bellow for AM, AT and SI, respectively:

$$E_p = -1.13 + 0.046\log(f)$$ Equation 3

$$E_p = -1.05 + 0.042\log(f)$$ Equation 4

$$E_p = -1.06 + 0.038\log(f)$$ Equation 5

So, according to these equations, the slope of experimentally curves were 46 mV, 42 mV and 38 mV, to AM, AT and SI, respectively, where considering $\alpha = 0.75$, typical value to fast redox reactions, and substituting the known values of R, F, and T, the room temperature, n was determined to be equal to 2 for all triazines, following a probably mechanism presented in *Supplementary data*. Electrochemical mechanisms for AM and AT are largely discussed in some previously works using HMDE and CuSAE [8, 15, 30].

The results obtained in this work were like abovementioned works, and for this can be ascertained that the most possible mechanism for the reduction of AM involved the reduction of bond carbon-SCH$_3$ and for AT is related to the reduction of bond carbon-chloride. Already, the SI mechanism is underexplored, but based in the analysis of the chemical structure and the results presented in this work, we can suppose that occurred a like mechanism AT, involving the reduction of bond carbon-chloride, as shown in *Supplementary data*. Finally, for subsequent experiments, 100 s^{-1} was selected as *f* parameters in all triazines analysis.

Finally, the other two parameters employed in SWV, *a* and ΔE_s were individually evaluated. SWV signals performed for *a* values from 5 to 50 mV, showed that the increase in *a* values promoted a linear increase in I$_p$ for all triazines. Considering E$_p$ values was observed that using 50 mV to *a* parameter was possible gain the best separation between peak reductions, and without considerable variations in the $\Delta E_{p1/2}$, as presented in the *Supplementary data*. This way, the 50 mV value was selected to posterior experiments, as suitable parameters to obtain sensitivity and selectivity in the proposed procedure.

For all triazines, the increase in the ΔE_s values promoted a decrease in the analytical signals accompanied by a considerable loss in the voltammetric profile definition, probably due to reduction in the number of points collected in the voltammograms construction, by use of Nova 2.1.2 software, as described in the *Experimental Section*. For this, 2 mV was selected as suitable scan increment in the posterior experiments.

3.4. Analytical parameters

The experimental (BR buffer, pH 2.5) and voltammetric (*f* = 100 s^{-1}, *a* = 50 mV and ΔEs = -2.0 mV) parameters were used in the construction of analytical curves to AM, AT and SI using DAE, considering the range concentration from 7.500x10^{-7} mol L^{-1} to 1.000x10^{-5} mol L^{-1}. For this, aliquots from the stock solution were consecutively added to the electrochemical cell, and for each addition SWV experiments were performed and the data collected were employed in the analytical curves built. These curves were developed in triplicate, to three triazines, and are shown in *Supplementary data*.

In Fig. 3 are shown the SWV plus the average analytical curve obtained to AM, where can be observed a linear increase in the voltammetric signals following the increase in the concentration added in the electrochemical cell, similar to observed in AT and SI

data. Besides, no was attained significative alterations in the E_p and $\Delta E_{p1/2}$ values due to increase in the concentration, for all triazines. The average approach to the linear adjusting can be represented by Equation 6, Equation 7 and Equation 8, considering the AM, AT and SI, respectively:

FIGURE 3

$$I_p(A) = -4.118x10^{-7}(\pm 4.511x10^{-7})(A) + 0.6801(\pm 0.1972) \text{ [AM]}(A / mol\,L^{-1}) \quad \text{Equation 6}$$

$$I_p(A) = 3.624x10^{-7}(\pm 3.429x10^{-7})(A) + 0.6584\,(\pm 0.4429) \text{ [AT]}(A / mol\,L^{-1}) \quad \text{Equation 7}$$

$$I_p(A) = -3.187x10^{-7}(\pm 1.011x10^{-6})(A) + 0.5029(\pm 0.4179) \text{ [SI]}(A / mol\,L^{-1}) \quad \text{Equation 8}$$

For each analytical curve equation, was calculated the confidence interval (CI) for interception and slope, according to:

$$CI = value \pm t\,s/\sqrt{n} \qquad \text{Equation 9}$$

where value is the medium value of the interception or slope, t is the tabulated t value considering assurance level of 99%, n is the number of determinations and s is the standard deviation of the interception or slope values. These calculus were performed and the values and are presented in Equation 6, Equation 7 and Equation 8, to AM, AT and SI respectively.

Furthermore, the average analytical curve of AM and SI presented a negative interception and of AT an interception different of zero. This way, significance test, the t-test, were realized in order to determine if the difference between the interception obtained in these analytical curves and the standard values originated from random error [32]. This calculous was performed according to:

$$t = (\overline{x} - \mu)\frac{\sqrt{n}}{s} \qquad \text{Equation 10}$$

where $\overline{x}$ is the average from interception values obtained, μ is the standard value expected in the case of the interception being zero, n is the number of determinations and s is the standard deviation of the current responses and the other symbols are similar to those used in the CI calculous. The $|t|$ value calculated were 9.02, 9.71 and 3.13 to AM, AT and SI, which was lower than the critical value ($t_{critical} = 9.92$) at an assurance level of 99%, indicating that no considerable differences occurred between the medium value calculated and the theoretical value, and the interceptions were free from random errors.

To attest the linearity from the curves presented above, was considerate the correlation coefficient (r), that presented value of the 0.9989, 0.9952 and 0.9963 for AM, AT and SI respectively, which indicate excellent linearity evidence (r> 0.99) [33].

The sensitivity of the proposed procedure was evaluated from the DL and QL calculous, as described in the *Experimental Section.* For this, were employed ten replicate blanks to calculate the mean value of the peak current related to the redox peak potential value of each triazine and the standard deviation of its values. The DL values individually calculated were 1.200×10^{-7} mol L^{-1} (27.28 µg L^{-1}), 1.241×10^{-7} mol L^{-1} (26.77 µg L^{-1}) and 1.624×10^{-7} mol L^{-1} (32.75 µg L^{-1}) for AM, AT and SI, respectively. Already, the QL calculated presented the following values: 3.636×10^{-7} mol L^{-1} (82.66 µg L^{-1}), 3.759×10^{-7} mol L^{-1} (81.07 µg L^{-1}) and 4.921×10^{-7} mol L^{-1} (99.24 µg L^{-1}) for AM, AT and SI, respectively.

These results presented values around one magnitude order higher than values previously published using HMDE or enzyme modified electrodes, which produce toxic waste or present irreversible inhibition of enzymes and excessive cost, respectively. However, with the proposed procedure in this work can be possible the detection of triazines in natural water samples, where the maximum values allowed by CONAMA (the National Counsel for the Environment – Brazil) for natural waters, is 100 µg L^{-1}, for any triazine-based pesticide [7]. Besides this, the DL and QL values calculated in this work were comparable with previously obtained using high-performance liquid chromatographic techniques [34, 35, 32], that employ sample preparation steps, promoting the increase in the costs and time of the analysis.

The precision was determinate by experiments of repeatability and reproducibility, as described *Experimental Section*, using a concentration of 2.00×10^{-7} mol L^{-1} of AM, AT and SI, separately, and the previously SWV optimized parameters. The reproducibility calculus were realized in the various days (*interday* precision), and calculated RSD values to AM, AT and SI were 2.58%, 4.24%, 4.75%, respectively. The repeatability experiments of the three triazines were realized at same time and same solution (*intraday* precision), and RSD values obtained were 2.13%, 3.56% and 2.62%, to AM, AT and SI, respectively. Thus, these values to RSD are indicative of the good precision of the proposed procedure [33].

Accuracy were assessed using recovery experiments, using the recovery curves performed by spiking a known concentration of the each triazine (2.00×10^{-6} mol L^{-1}, where

[triazine]_added) was individually added in electrochemical cell, followed by standard addition method, in the pure supporting electrolyte, in which the voltammetric signals were evaluated [33]. The recovery percentages were used to evaluate and quantify the triazines that was added. In this way, the recovery concentration ([triazine]_recovered) was identified graphically, with the abscissa axis denoting the concentration of each triazine in the electrochemical cell. Extrapolating the curve along this axis yields the artificially spiked concentration, allowing for the calculation of the recovery values (%R), as shown in Eq. 11:

$$\%R = \frac{[\text{triazine}]_{\text{recovered}}}{[\text{triazine}]_{\text{added}}} x100 \qquad\qquad \text{Equation 11}$$

Recovery curves were built in triplicate, and the average %R obtained was 100.5%, 100.2% and 99.6% to AM, AT and SI, respectively. These results presented values in a suitable range for analytical applications, which are acceptable values from 70 to 130% for recovery percentages [25], indicating that the proposed procedure can be successfully applied in the analytical determination of AM, AT and SI, with good efficiency and accuracy in the analytical results.

Finally, all analytical results obtained and discussed above are presented in Table 1, indicating an abstract with all merit figures for the analytical determination of AM, AT and SI employing DAE allied to SWV. Thus, these data corroborate that the proposed methodology provides a suitable alternative method for the electrochemical determination of triazines, and the traditional mercury electrodes can be substitute by an environmentally friendly sensor, without waste toxics generations, or the use of high cost instrumentation with pre-treatments necessity of the samples typical of the use of high-performance liquid chromatography.

TABLE 1

3.5. Analytical applications

In Alto Paranaíba region, Minas Gerais states, Brazil, live an intensive use of triazines-based pesticides in agricultural practices, similar to occurs in other Brazil regions and other countries. For this, the procedure presented above was applied in the analysis of natural water samples collected from three points of the Paranaíba river, as described in the *Experimental section*. These samples were characterized by BOD analysis, that indicated the presence of the 10.8 mg L^{-1}, 11.6 mg L^{-1} and 15.4 mg L^{-1}, of total organic compounds,

considering the sample 1, sample 2 and sample 3, respectively, which are directly related to different levels of organic matter, including wastes from agricultural, industrial and urban activities.

All water samples were used as received, with only a simple filtration to remove solid particles. 1.0 mL of each sample was added in electrochemical cell containing 9.0 mL of BR buffer pH 2.5 and the analytical curves were again built by SWV experiments on the DAE. In this way, the influences of sample chemical composition were evaluated. The analytical curves obtained under these new experimental conditions are presented in Fig. 4 considering all triazines. These experiments were performed only to evaluate the interferences of the components samples in the analytical signals, and for this, the authors considerate that the samples no contained none triazine. This way, the efficiency of the proposed procedure was observed in complex samples, characterized by different BOD values.

FIGURE 4

Considering the curves presented in Fig. 4 can be observed that the increase in the BOD values promoted a similar increase in the slope of the analytical curves, indicating that probably the components present in each sample also were reduced in the same interval potential of the triazines, or these components interact with the triazines, promoting a improvements in the analytical signals, or the possible metals present in each sample can be complexed by each triazine molecule, which also were reduced promoting increase in the analytical signals.

Additionally, to AM and SI, that involved redox reaction controlled by diffusion rate of electroactive species to bulk solutions to interface electrode, the effects of components samples in the analytical signals were lower than effects in the AT responses, which involves reactants adsorption process as determining steps in the redox reaction. The results of linear regression from the straight lines obtained presented in Figure 4 are shown in Table 2, jointly with the DL and QL values calculated for each sample and each triazine. These results indicated that the proposed procedure enable detect AM, AT and SI in natural water samples with a range concentration interval, suitable linearity, and also around or bellow of the maximum level permitted by specify legislations [7].

TABLE 2

Recovery experiments were also performed in order to evaluate the interference of organic and inorganic components in natural water samples. Samples were artificially

spiked with 2.000×10^{-6} mol L^{-1} of each triazine, with individual experiments performed using the proposed procedure and the standard addition method. The recovery data, for all triazines, shown in Table 3, presented values around to values obtained in pure electrolyte, showing this way, that the components of the samples practically not interfered in the voltammetric signals and the proposed procedure is suitable in the electroanalytical determination of triazines-based pesticides in natural waters.

TABLE 3

4. CONCLUSIONS

The DAE was constructed using a very simple procedure, like employed in dental clinics, that produced a surface with compact and globular crystals. Physical characterization indicated the chemical composition and the morphology, that confirmed the quantities of each components and the predominance of Ag_2Hg_3 and Ag_3Hg_2 phases, without mercury or silver free, evidencing the obtention of an environmentally friendly sensor.

The experimental (supporting electrolyte and pH of the medium) plus the voltammetric (f, a and ΔE_s) parameters were optimized in order to obtain the best voltammetric responses, considering sensitivity and selectivity. The use of BR buffer pH 2.5, with $f = 100$ s^{-1}, $a = 50$ mV and $\Delta E_s = -2$ mV proportionated a single and well-defined irreversible redox voltammetric peaks, that were related to two electron-transfer, in which to AM corresponded to reduction of the carbon-SCH$_3$ bond and to AT and SI are related to reduction of the carbon-chloride bond, similar to previously observed by use of traditional mercury or copper solid amalgam electrodes.

Analytical parameters such as: linear range concentration, correlation coefficient, slope of the analytical curve, confidence interval, detection and quantification limits, relative standard deviation and recovery percentages were calculated in pure electrolyte allowing suitable sensitivity and selectivity, associated with an elevated level of repeatability and reproducibility. So, the proposed procedure was applied with success in determining AM, AT and SI in spiked natural water, which presented different degrees of pollution from agricultural, urban and industrial activities, determinate by BOD.

Thus, the novelty of the proposed methodology is rooted in the use of DAE as voltammetric sensor to triazines-based pesticides detection in natural waters, without any

pre-treatment or extraction procedure or the use of chemically modified surfaces or the use of mercury as voltammetric sensor.

Acknowledgments

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TABLES

Table 1: Analytical parameters for the determination of triazines in pure electrolyte on DAE, where LR is the linearity range, r is the correlation coefficient, CI is the confidence interval, DL and QL are detection and quantification limit, respectively.

Parameter	Ametryn	Atrazine	Simazine
LR (μmol L^{-1})	0.7500 – 10.00	0.7500 – 10.00	0.7500 – 10.00
r	0.9989	0.9952	0.9963
Intercept (A)	-4.118x10^{-7}	3.624x10^{-7}	-3.1869x10^{-7}
Slope (A / mol L^{-1})	0.6801	0.6584	0.5029
CI of intercept (A)	$\pm$4.511x10^{-7}	$\pm$3.429x10^{-7}	$\pm$1.011 x10^{-6}
CI of slope (A / mol L^{-1})	$\pm$0.1972	$\pm$0.4429	$\pm$0.4179
S_b (A)	2.475x10^{-8}	2.475x10^{-8}	2.475x10^{-8}
DL (mol L^{-1})	1.200x10^{-7} (27.28 μg L^{-1})	1.241x10^{-7} (26.77 μg L^{-1})	1.624x10^{-7} (32.75 μg L^{-1})
QL (mol L^{-1})	3.636 x10^{-7} (82.66 μg L^{-1})	3.759 x10^{-7} (81.07 μg L^{-1})	4.921 x10^{-7} (99.24 μg L^{-1})
Repeatability (%)	2.13	4.25	4.75
Reproducibility (%)	2.58	3.56	2.62
Recovery (%)	100.5	100.2	99.6

Table 2: Analytical parameters for the determination of triazines in natural water samples using DAE allied to SWV, where LR is the linearity range, r is the correlation coefficient, and DL and QL are detection and quantification limit, respectively.

Sample	LR (μmol L^{-1})	r	Slope (A / mol L^{-1})	DL (μmol L^{-1})	QL (μmol L^{-1})
			Ametryn		
1	0.7500 - 10.00	0.9824	0.1806	0.4522 (102.8 ppb)	1.370 (311.4 ppb)
2	2.000 - 10.00	0.9684	0.2424	0.4070 (92.52 ppb)	1.2334 (280.4 ppb)
3	0.7500 - 10.00	0.9932	1.194	0.0068 (1.546 ppb)	0.2072 (47.01 ppb)
			Atrazine		
1	0.7500 - 10.00	0.9959	0.08140	0.1003 (21.63 ppb)	0.3041 (65.59 ppb)
2	0.7500 - 10.00	0.9900	0.08249	0.9901 (213.5 ppb)	3.000 (647.00 ppb)
3	0.7500 - 10.00	0.9474	0.1585	0.5153 (111.1 ppb)	1.562 (336.8 ppb)
			Simazine		
1	0.7500 - 10.00	0.9909	0.1288	0.6341 (127.9 ppb)	1.921 (387.4 ppb)
2	0.7500 - 10.00	0.9903	0.3316	0.2462 (49.65 ppb)	0.7463 (150.5 ppb)
3	0.7500 - 10.00	0.9953	0.4078	0.2003 (40.39 ppb)	0.6069 (122.2 ppb)

Table 3: Analytical parameters obtained in natural water samples for AT, AM and SI detection using DAE allied to SWV. The same parameter evaluated in supporting electrolyte, and with data were evaluated using medium values from three recovery curves. The numbers 1, 2 and 3 correspond to each sample employed.

	Ametryn			Atrazine			Simazine		
	1	2	3	1	2	3	1	2	3
Added (μmol L^{-1})	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Recovered (μmol L^{-1})	2.117	2.196	1.952	2.188	2.132	2.044	1.786	2.060	2.197
Recovery (%)	106	110	98	109	107	102	89	103	110

FIGURE CAPTIONS

Figure 1: Square wave voltammograms for reduction of the 1.00×10^{-5} mol L^{-1} of AM, AT and SI on the DAE using BR buffer with different pH values and $a = 50$ mV, $\Delta E_s = -2$ mV and $f = 100$ s^{-1} and its respective chemical structures as insert. Relationships between I_p and E_p with pH values.

Figure 2: Square wave voltammograms for reduction of the 1.00×10^{-5} mol L^{-1} of AM, AT and SI on the DAE using BR buffer pH 2.5 with $a = 50$ mV, $\Delta E_s = -2$ mV and different values of f. Inserts show the relationships between I_p and f values for each triazine.

Figure 3: Square wave voltammograms for reduction of AM on the DAE using BR buffer pH 2.5 with $f = 100$ s^{-1}, $a = 50$ mV, $\Delta E_s = -2$ mV, in the range concentration from 7.500×10^{-7} mol L^{-1} to 1.000×10^{-5} mol L^{-1}. Insert correspond to average analytical curve.

Figure 4: Analytical curves obtained to AM, AT and SI in the range concentration from 7.500×10^{-7} mol L^{-1} to 1.000×10^{-5} mol L^{-1} in BR buffer pH 2.5 and three water samples (sample 1, sample 2 and sample 3), and using DAE allied to SWV with $f = 100$ s^{-1}, $a = 50$ mV, $\Delta E_s = -2$ mV.

FIGURES
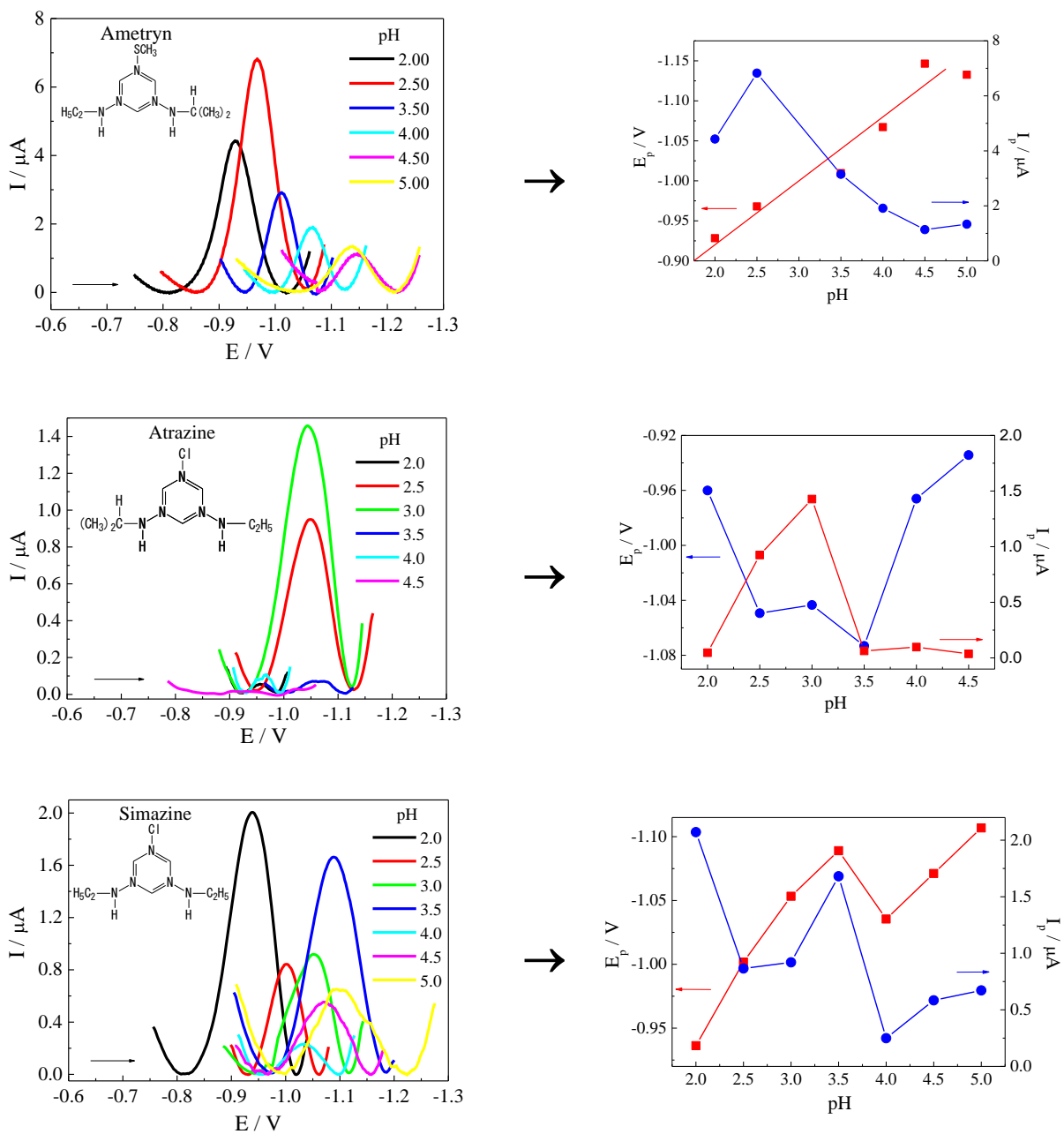
Figure 1: F. C. O. L. Martins and D. De Souza
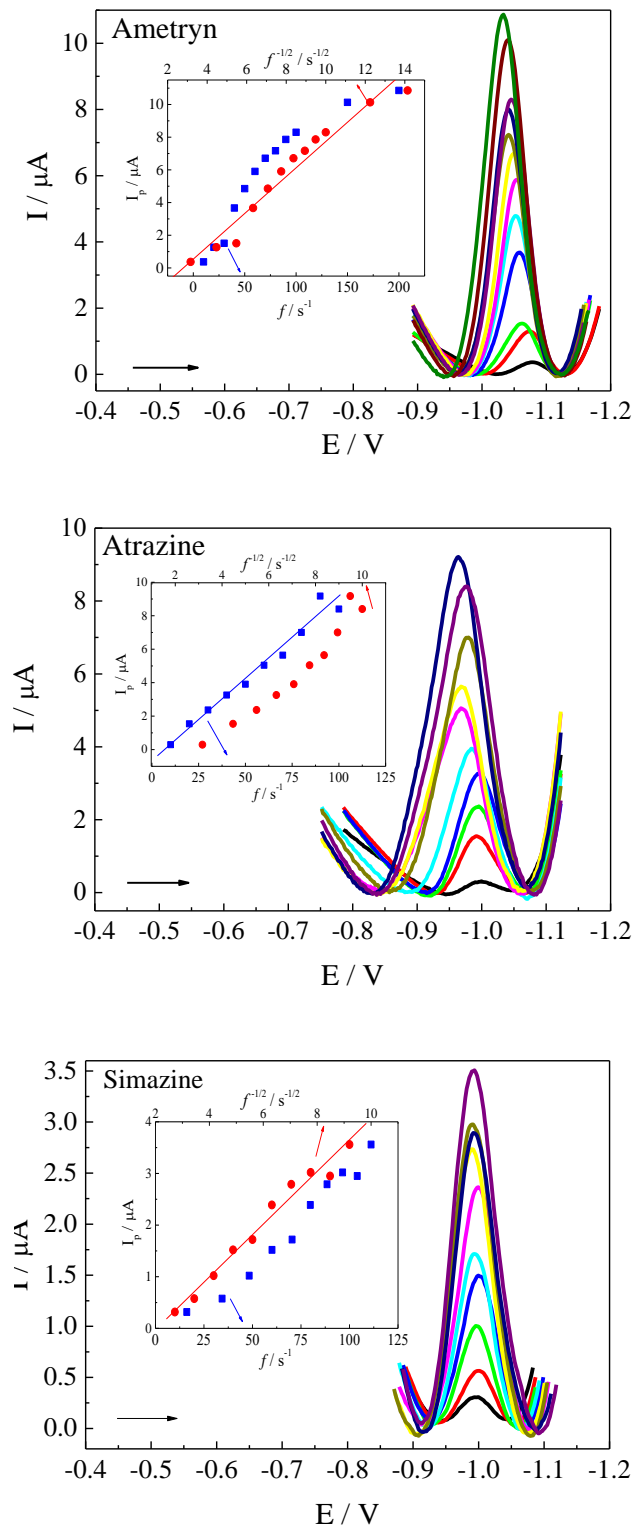
Figure 2: F. C. O. L. Martins and D. De Souza

The inset plot shows:

$$I_p = -4.118 \times 10^{-7}(A) + 0.6806 C(A/mol\ L^{-1})$$

$$r = 0.9989$$
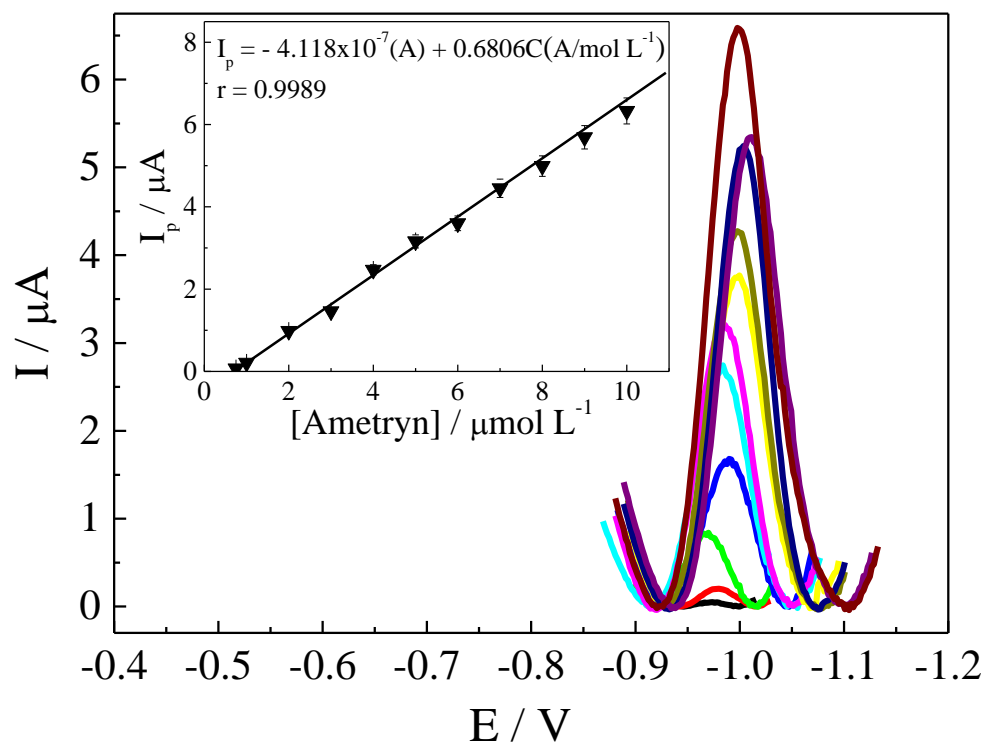
Figure 3: F. C. O. L. Martins and D. De Souza
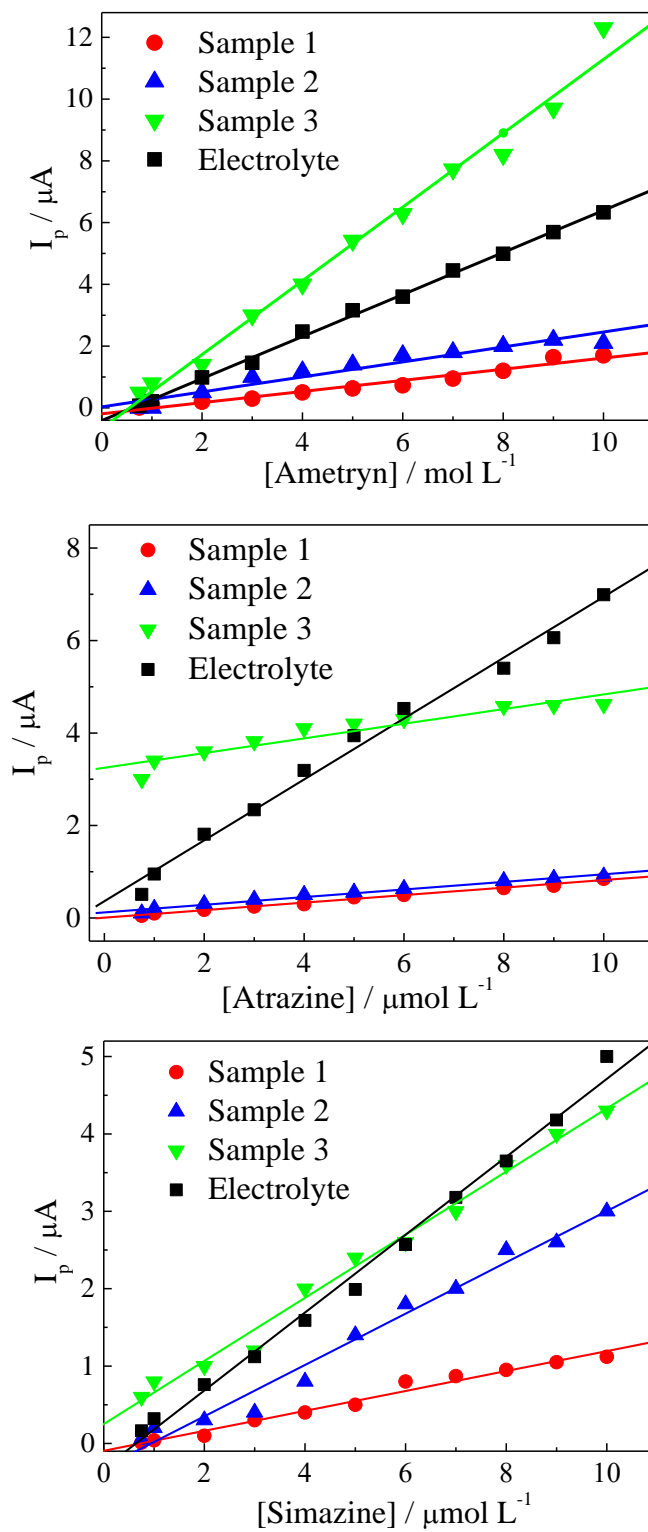
Figure 4: F. C. O. L. Martins and D. De Souza

Supplementary Data

for

Dental amalgam electrode as voltammetric sensor for triazine-based determinations: application in natural water samples

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Table of contents:

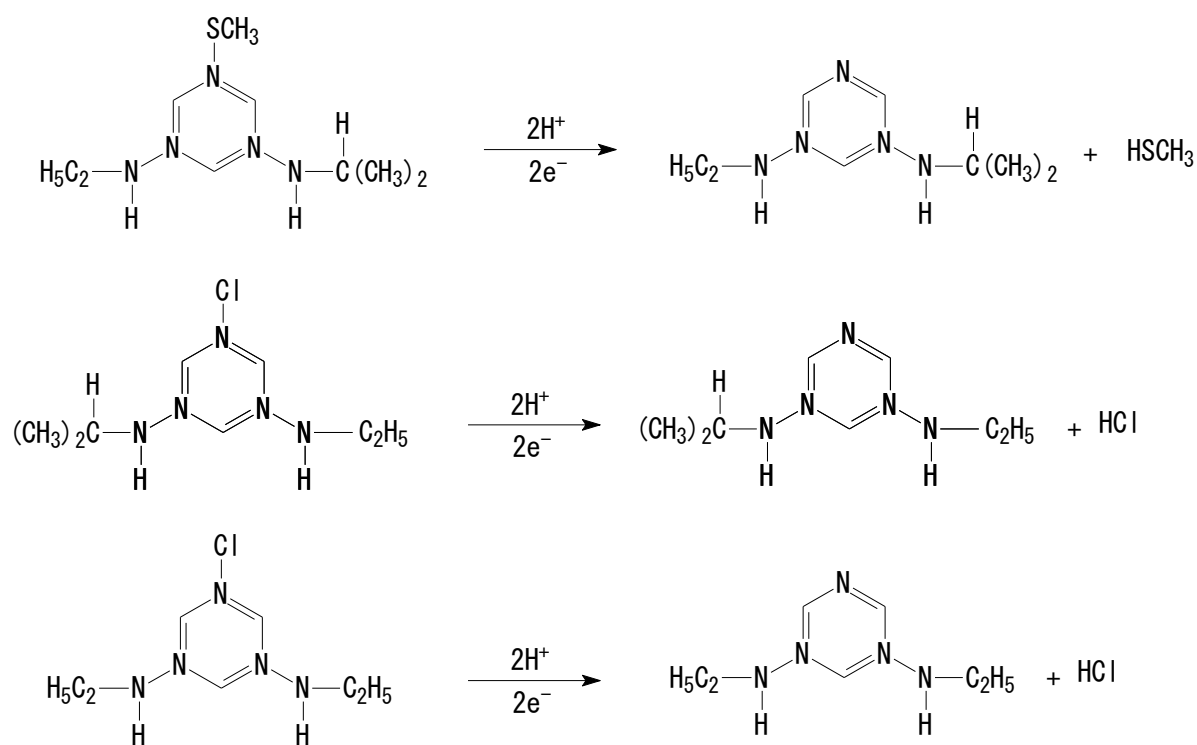(a)   (b)

Fig. S1: Scanning Electron Microscopy images of DAE with magnification of the x1000 (a) and
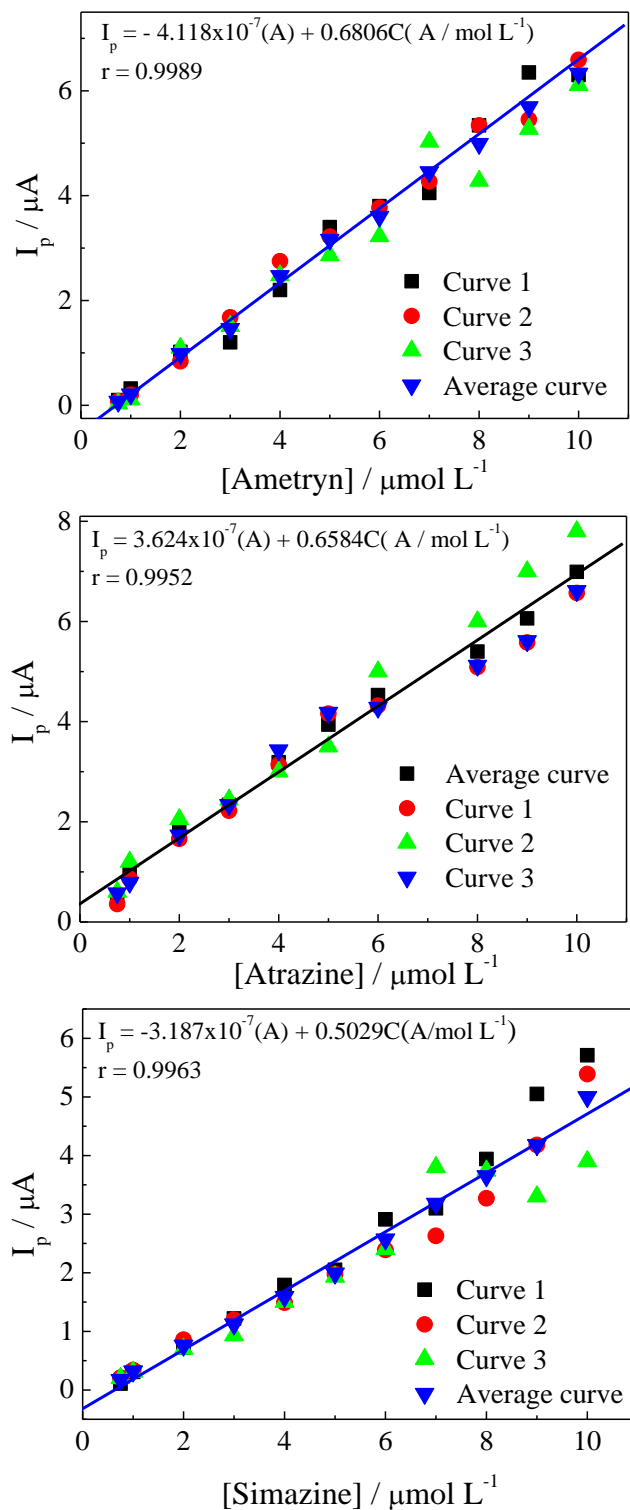x5000 (b).
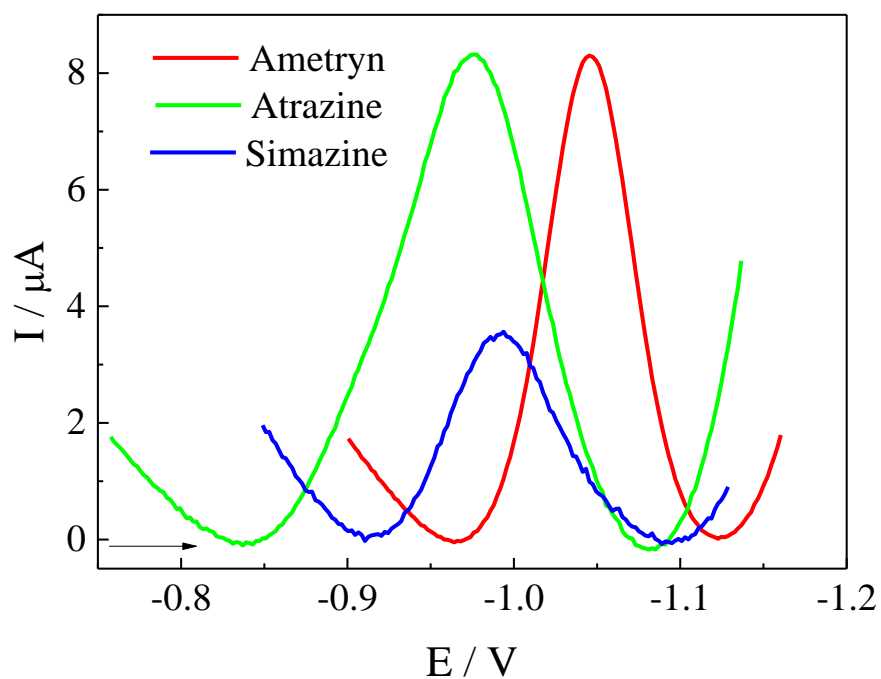
Fig. S2: Square wave voltammograms for reduction of the 1.00×10^{-5} mol L^{-1} of AM, AT and SI in the DAE using BR buffer pH 2.5 with $f = 100$ s^{-1}, $a = 50$ mV, $\Delta E_s = -2$ mV, obtained after the optimization of the DAE electrochemical regeneration procedure.

Fig. S3: Proposed mechanisms for electrochemical reduction reaction of the AM, AT and SI under the DAE.
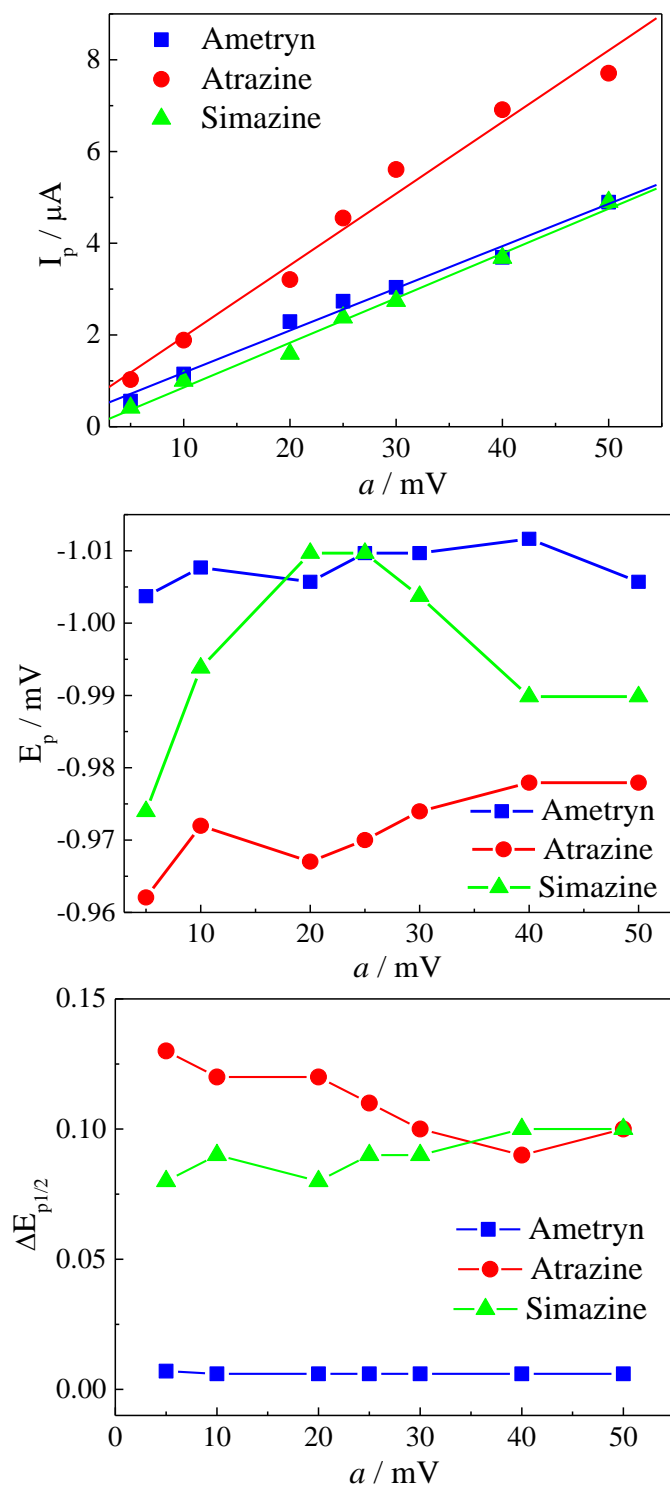
Fig. S4: Relationships between I_p, E_p and $\Delta E_{p1/2}$ with a for AM, AT and SI obtained from square wave voltammograms for reduction of the 1.00×10^{-5} mol L^{-1} in the DAE using BR buffer pH 2.5 with $f = 100$ s^{-1} and $\Delta Es = -2$ mV.

Fig. S 5: Average of the analytical curves for AM, AT and SI obtained from square wave voltammograms for reduction of triazines on the DAE using BR buffer pH 2.5 with $f = 100$ s^{-1}, $a = 50$ mV, $\Delta E_s = -2$ mV.