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Multiple square wave voltammetry for analytical determination of paraquat in natural water, food, and beverages using microelectrodes

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Abstract

This paper reports on the use of multiple square wave voltammetry (MSWV) for analytical determination of paraquat herbicide at gold microelectrode (Au-ME) in different samples of natural water, food, and beverages. In this work, the MSWV consisted in a sequence of four pairs of potential pulse in the same step and the interval potential evaluated was of the 0.0 V at −1.2 V versus Ag/AgCl 3.0 mol L^{-1}. The paraquat herbicide presented two reduction peaks, in −0.69 V and −0.99 V, with profile of the redox process totally reversible, and the use of multiple pulses allowed a detection of nanomolar levels after the optimization of experimental and voltammetric conditions. Analytical curves were constructed for pulse potential frequency of 250 s^{-1}, pulse amplitude of 50 mV, scan increment of 2 mV and pulse number of 8 pulses in a same step. The two reduction peaks showed that the peak currents were found to be directly proportional to the pesticide concentration in the range comprised between 5.0×10^{-7} mol L^{-1} and 1.04×10^{-5} mol L^{-1}. With this, it was possible to determine detection limits (DL), which resulted in 0.044 μg L^{-1} (0.044 ppb) and 0.146 μg L^{-1} (0.146 ppb), respectively, for peak 1 and peak 2. DL results, obtained using MSWV, were 2–3 orders of magnitude lower (10^{-2} to 10^{-3}) less than those observed for traditional square wave voltammetry or published in literature, clearly pointing to the advantages arising from the possibility of using a MSWV for analytical purposes in contaminated matrices. In addition, the proposed methodology was applied in different samples of natural water, food and beverages without pre-treatment or pre-concentration step, where a recovery measurement indicated that the methodology could be employed to analyze paraquat in such matrices.

Keywords: Multiple square wave voltammetry; Microelectrodes; Pesticides

1. Introduction

The development of electronic components has promoted recent innovations in the electroanalytical instrumentation, generating new possibilities for the use of some techniques in order to increase the signal-to-noise ratio and to lower detectable concentration of the organic and inorganic species in different samples, using different electrodic surfaces. Among the electroanalytical techniques, the "classical" pulse voltammetry, such as the differential pulse or square wave voltammetry, has been successfully employed for analytical [1–5] and mechanistic purposes [6,7] in the last few years.

In order to obtain the lower detection limits at nanomolar levels, the use of an extremely sensitive electroanalytical technique named multiple square wave voltammetry (MSWV) can be employed. The MSWV is a multipulse technique whose perturbation mode is similar to the square wave voltammetry (SWV) [6,8–10], but with the difference that onto each step of the staircase, it can be applied more than one pair of potential pulses of opposing sign [11–13]. The voltammograms present profile similar to those obtained for SWV and the response is produced in a few seconds, in which the sampling or integration of the currents is carried out on each step of the staircase, from the difference between the sum of the response which was measured during the forward pulse, and the sum of the response which was measured during the reverse pulse.

This mode of multiple pulse potential application is suitable to substitute SWV in the electroanalytical analysis of inorganic and metallorganic compounds since its use allows for the improvement of the analytical sensitivity to about 2–3 orders of magnitude and it has been successfully applied for trace analysis even in complex samples [13–17].

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Recent works, reported in the literature, have shown several applications and electroanalytical methodologies employing microelectrodes (ME) as working electrodes [18–21]. Their application and construction have been intensively increased, year after year, and the number of works and reviews about construction, characterization and application of the ME has been considerable in the last decade [22–27] due to the innumerable advantages presented and, especially, for the several possibilities of the use with improvement in the analytical response.

The properties related to the small size of the ME allowed their use in the study of the reactions and electrodic process in lower conductivity solvents and in the absence of the support electrolyte; it minimizes the cost and the manipulation of the samples. The study of the fast transference electronic processes and chemistry-coupled reactions is made easy by the use of the ME. Moreover, this use can be applied for investigation in a great variety of experiments, previously impossible with conventional electrodes, such as "in vivo" analysis [28]. As a consequence of these properties, the ME can be used in the analytical determination of pesticides in different samples, without pre-treatment or clean up steps, thus offering an excellent alternative to the use of the chromatographic techniques.

The paraquat herbicide (1,1′-dimethyl-4,4′-dipyridinium chloride), also known as methyl viologen, is one of the most toxic substances used in agriculture in several countries [29]. Paraquat is a dipyridiliun herbicide that is utilized to weed control in many crops and there have been many authenticated cases of detection of its residues in water sources [30] and its residues consist in a potential danger to health, since it is a highly persistent molecule when present in the environment and this fact increases the contamination risk from abusive utilization.

Due to its continuous use, paraquat has been extensively investigated. Electrochemically, paraquat has been analyzed on different electrode surfaces, i.e., noble metals [20], mercury [31] and chemically modified [32] electrodes, which makes the behavior of this molecule a well-known electrochemical system.

The purpose of this work is to study the applicability of multiple square wave voltammetry together with gold microelectrodes in the electroanalytical determination of paraquat in natural waters, lemon and orange juices, apple, potato and sugar cane, without any pre-purification or preparation step of the sample.

2. Experimental

2.1. Reagents and equipment

A 1.0×10^{-3} mol L^{-1} stock solution of paraquat (Aldrich 98%) was prepared using Milli-Q (Millipore) Corporation water. For the measurements with gold microelectrode (Au-ME), a 0.1 mol L^{-1} Na_2SO_4 electrolyte (adjusted by adding the appropriate amount of a 0.1 mol L^{-1} NaOH and H_2SO_4 electrolyte solutions) was used as the support electrolyte.

SWV and MSWV were carried out with a PGZ 402 Voltalab potentiostat of the Radiometer Analytical coupled to Voltamaster 5.06 software also of the Radiometer Analytical.

A 3.0 mol L^{-1} Ag/AgCl electrode was used as the reference electrode while the working electrodes were lab-made and constructed with gold micro wires. Before each experiment, a stream of N_2 was passed through the solution for 10 min.

2.2. Principle of the pulse mode

Fig. 1 shows the mode of pulse potential employed according to Chevalet et al. (A) and the mode used in present work (B), where N is the pulse number superimposed in each step, a the pulse amplitude, ΔE_s the scan increment, τ the duration of the each pulse, Δt the time of stabilization of double layer, u the duration of pulse direct, and v the duration of pulse reverse. In mode defined in (A) in each transition a the system entry in equilibrium for time Δt, after this the intensities of current direct (u) and reverse (v) are integrated. The some of the N pulses constituted the Q_1 measured that to correspond to the response in the step. For each step, the procedure is repeated and the response is constituted by sum of all charges.

In mode (B) the measured of current is evaluated in the final of the pulse direct and pulse reverse, similar to traditional SWV. This way the capacitive current is totally negligenciable and the faradaic current is the maxim improvement the ratio signal/noise and consequently the analytical sensitivity.

2.3. Microelectrodes construction and characterization

The Au-ME was constructed from a 25 μm diameter gold wire (Goodfellow). The micro wire was inserted into a piece of glass tube of approximately 0.5 mm internal diameter which was later filled with Epoxy resin. After the hardening of the Epoxy resin, the Au-ME was polished using a mechanical polisher and glasspaper of different granulations. After this polishing procedure, the Au-ME was cleaned with water and a disk surface was observed.

The voltammetric characterization was carried out by studying the electrochemical response of the potassium hexacyanoferrate (III) solutions in acid medium because its behavior is well known and the voltammograms exhibit sigmoid profiles, characteristic of the utilization of ME [33].

2.4. Working procedure

All measurements were carried out under ambient conditions. A two-electrode configuration was used with the reference electrode (Ag/AgCl 3.0 mol L^{-1}) acting also as counter electrode. The appropriate solutions were transferred into the electrochemical cell and the optimization of the analytical procedure for MSWV was carried out following a systematic study of the experimental parameters that affect the SWV responses, such as, the pH of the medium, the pulse potential frequency (f) related to total pulses duration, the pulse height (a) and the height of the potential step (ΔE_s) or scan increment. These parameters were properly optimized since their values exert deep influence on the sensitivity of voltammetric analysis [6,10]. The mentioned

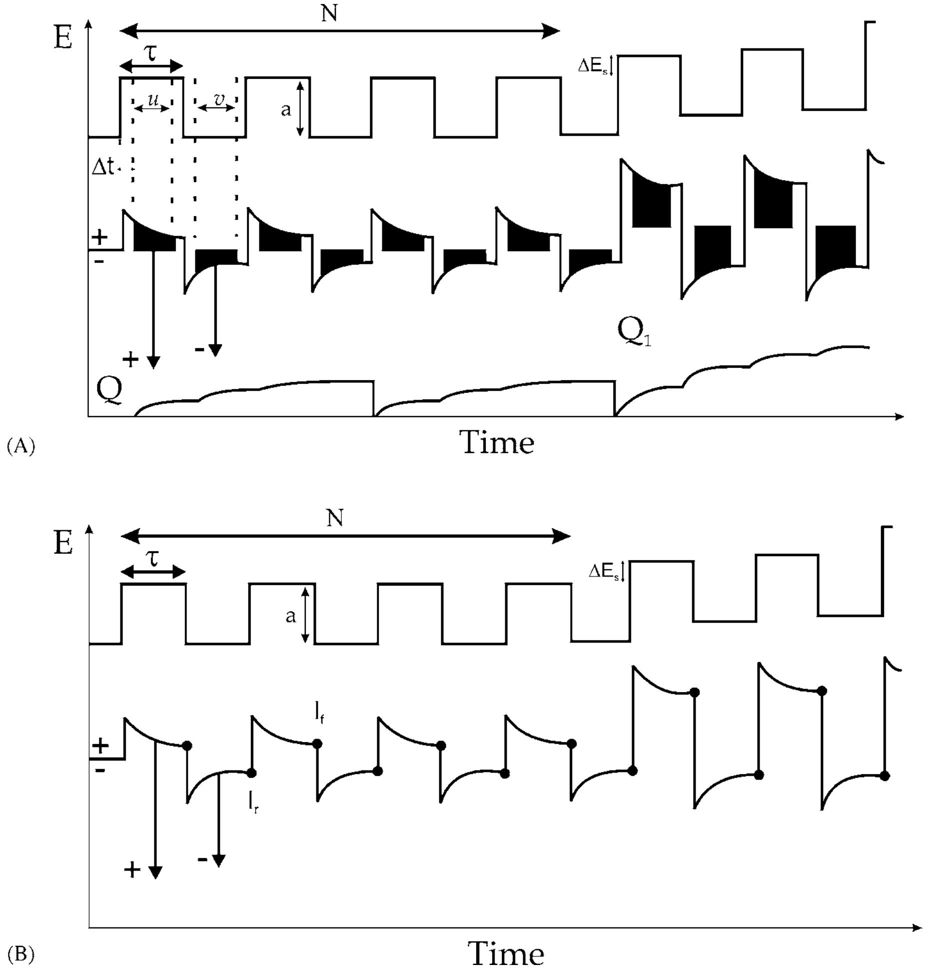

Fig. 1. Mode of pulse potential application, according to Chevalet (A) and used in this work (B).

parameters were optimised in relation to the maximum value of peak current and the maximum selectivity (half-peak width). Additionally, the number of superimposed pulses in each step (*N*) was also evaluated.

To accomplish the abovementioned, the working electrode was placed in the measuring cell filled with 10 ml of a Na_2SO_4 0.1 mol L^{-1} solution containing a known concentration of pesticide after which the experimental and voltammetric parameters were studied. For the measurements, several support electrolytes were initially tested and the best results obtained for 0.1 mol L^{-1} Na_2SO_4.

The multiple square wave voltammetry was programmed using the universal pulse procedure to present in software Voltamaster 5.06 of the Radiometer Analytical which permitted the generation of 1–8 pulses (or levels) superimposed on a potential step between two applied potential set points. In using the software, each step is applied based on a reference level. Values of currents were measured for each applied pulse and the differential current (direct–reverse), measured in the superior limiting point.

In all experiments, the electrochemical cell was placed in a Faraday cage in order to minimize background noise. Before initiating the analysis, some cyclic voltammetries at fast rate were realized in a support electrolyte for best results of the ME.

After the optimization of voltammetric parameters, analytical curves were obtained in pure electrolyte by the standard addition method. The standard deviation of the mean current (S_b) measured at the reduction potential of paraquat for 10 voltammograms of the blank solution in pure electrolytes was used [34,35] in the determination of the quantification and detection limits (QL and DL, respectively) together with the slope of the straight line of the analytical curves (*b*) as follows:

$$\mathrm{QL} = \frac{10S_b}{b} \tag{1}$$

$$\mathrm{DL} = \frac{3S_b}{b} \tag{2}$$

The recovery experiments were carried out by adding a known amount of paraquat to the support electrolyte followed by standard additions from the paraquat stock solution and plotting the resulting analytical curve. All measurements were performed in triplicate. The recovery efficiencies (%*R*) were calculated using Eq. (3); here, the value [paraquat]found refers to the concentration obtained by extrapolating the analytical curve of the corresponding spiked samples:

$$\%R = \frac{[\text{paraquat] found}}{[\text{paraquat] added}} \times 100 \tag{3}$$

The precision and accuracy of methodologies were tested with different standard solutions of paraquat and the relative standard deviations (R.S.D.) were calculated as follows:

$$\text{R.S.D.} = \frac{S_b}{\overline{X}} \qquad (4)$$

where S_b is standard deviation of the mean current values obtained and $\overline{X}$is the mean peak current value.

2.5. Application of methodology

To attest the applicability of the proposed methodology, the effect of interference was evaluated using natural water samples taken from river Mogi-Guaçu situated in the state of São Paulo, Brazil. The samples were collected from three different points of the river, namely, Cepta (point 1), in the Cachoeira de Emas (point 2) and at Guajari (point 3). The sampling points presented different characteristics with regard to the level of pollution characterized by chemical and biologic oxygen demand. The electrolytes were prepared by dissolving Na_2SO_4 in both pure or natural water, and the measurements performed without pre-treatment of the solutions.

The aforedescribed methodology was also applied to sugar cane, lemon and orange juice, apple and potato samples. All samples were used directly for experiments, without pre-treatment or separation step, only adjusting the pH of the solution to 6.0 with NaOH solution. These experiments were performed to evaluate the matrix interference effect in the application of the methodology in complex samples.

For apple and potato, 20 g of each sample were transferred to an electrochemical cell and spiked with the appropriate concentration of paraquat stock solutions. Next, the mixture was mechanically stirred and electrochemical measurements were evaluated, under the experimental conditions described above, and by applying the standard addition method which involved successive additions of a 2.33×10^{-7} mol L^{-1} and 8.71×10^{-7} mol L^{-1} paraquat stock solution.

Orange and lemon juices were extracted from their respective fruits and 10 ml of each juice with pH values adjusted were transferred to an electrochemical cell and artificially contaminated with a known amount of paraquat and recovery measurements performed. All experiments were performed in triplicate. The sugar cane juice samples were acquired in local commerce and the same procedure used to other juices samples was also applied for this sample.

Before the experiments in the different samples, the microelectrode was polished with ultra fine glass paper for to remove interferences adsorbed in the surface of the microelectrode.

3. Results and discussion

3.1. Electrochemical behavior

According to previous work [36], the square wave voltammograms obtained for paraquat herbicide present two voltammetric peaks towards the negative sweep direction, the first one around −0.7 V and the second at approximately −1.0 V versus Ag/AgCl 3.00 mol L^{-1}. Based on this work, the electrochemical process related to peaks present a totally reversible behavior indicated by the presence of direct and reverse currents with similar values of peak current. In addition, the difference between peak potential for forward and reverse scan, presented values about 60 mV, which is indicative of the transfer of one electron during the redox process, a behavior similar to that published in other literature reports [20,31,32]. The two peaks can hence be used, with great success, for electroanalytical determinations of paraquat residues in different samples.

3.2. Optimization of experimental parameters

In order to optimize the MSWV, a previous study was realized of the relationships between peak current (I_p) and peak potential (E_p) with the parameters of the SWV, like frequency of the pulse potential (f), amplitude of the pulse (a) and scan increment (ΔE_s). The proton concentration in the support electrolyte was also initially evaluated. All these parameters exert an intense effect on the peak current or peak potential.

The decrease in proton concentration as pH increases from 2.0 to 9.5 is shown to have a pronounced effect on the SWV response of paraquat. Up to a pH of 6.0, the peak currents show a fivefold increase for peak 1 and a threefold for peak 2. The peak potentials do not, however, seem to be affected by the concentration of H^+, suggesting the absence of any protonation step in the reduction mechanism, which is in close agreement with published works [31,32]. Therefore, pH 6.0 was chosen for subsequent measurements.

The effect of f on the I_p and E_p of paraquat on Au-ME was evaluated. In this study, the square wave voltammograms demonstrated that for either peak 1 or 2, increasing f values lead to an increase in I_p, but the relation between I_p and f being different for both peaks. For peak 1, the values of I_p are directly proportional to the square root of f, while for peak 2, they show a linear relation to f. According to criteria for diagnosis using SWV, the behavior of peak 1 is characteristic of a reaction in solution and peak 2 involves adsorption as the rate determining step [20]. For both peaks, the intensities I_p increased for values of f up to 1000 s^{-1} without any loss of quality in the electrochemical signal. Nevertheless, the maximum acceptable value to be in an MSWV program, which is 250 s^{-1}, corresponds to 0.004 s of duration for each step, was used in the present experimental study. This value was used in the study of the pulse number and in the application of the electroanalytical methodology.

The amplitude of the pulse was also considered. In the case of the reduction of paraquat on Au-ME, the results obtained for both peaks demonstrated that an increased in values of a promoted a linear increase in the peak current values. As expected from SWV theory [9,10], the values of I_p show a nearly linear variation with the pulse amplitude for values of a from 5 mV to 50 mV, while in practice, there E_p shows no variation as a function of a. Both behaviors, however, point to a reversible redox process. For analytical applications, a value of 50 mV was chosen for a.

Therefore, as expected, an increase in scan increment will also increase the signal and the sensitivity of the technique. Meanwhile, for large values of ΔE_s, a widening of the peaks may occur thus diminishing the resolution of the analysis. For this reason, ΔE_s was evaluated for the reduction of paraquat. Results obtained for both peaks show that, except for peak 2, the increased in ΔE_s does not have any influence on the peak potentials. In this case, an increase in ΔE_s results in a decrease in I_p, which indicate an adsorption process for peak 2. This behavior is confirmed by previous results obtained in the study of the relation between frequency of pulse potential and I_p. In subsequent experiments, a value of $\Delta E_s = 2$ mV was adopted.

After optimization of the experimental and voltammetric parameters using the SWV, the number of pulse potential in each step, (N), was also studied. In principle, the effect of increasing N should be an increase in the voltammetric signal, thus resulting in an improvement in analytical sensitivity [12–17].

A series of multiple square voltammograms obtained for the reduction of paraquat on Au-ME when N is varied from 2 to 8, which is the range provided for the instrument and the software used showed that the relation between I_p and N for the two peaks for the reduction of paraquat on Au-ME was linear, and consequently an increase in N produces a better analytical signal, for both peaks, demonstrating the great improvement in signal, as expected when multiple pulses were used. Based on these observations, analytical curves of the MSWV were constructed using 8 pulses potential in each step.

Fig. 2 presents the relationships between the peak current and voltammetric parameters obtained for paraquat reduction on Au-ME, where it is possible to observe the aspects that were mentioned above.

3.3. Analytical methodology using MSWV

Using the optimized parameters above, calibration curves were obtained for paraquat on an electrolyte prepared with pure electrolyte. For this, aliquots from the stock pesticide solution were consecutively added to the electrochemical cell. The MSWV responses were recorded for a range of concentration of 5.0×10^{-7} mol L^{-1} to 1.04×10^{-5} mol L^{-1} with $f = 250$ s^{-1}, $a = 50$ mV, $\Delta E_s = 2$ mV and $N = 8$. The multiple square wave voltammograms and the linear relationships between peak currents and concentrations added are presented in Fig. 3 for both peaks.

From Fig. 3, the detection (DL) and quantification limits (QL) were obtained for the experimental conditions employed the criterions presented in Section 2. Table 1 shows the experimental results obtained, where the equations for analytical curve, the correlation coefficient (r), which determines the degree of linearity of the relationship between the concentration of pesticide and peak current, the standard deviation of the arithmetic mean of 10 blank solutions (S_b), the slope of the working curve (s), the detection limit (DL) the quantification limit (QL), and the analytic sensitivity of the MSWV for peaks 1 and 2.

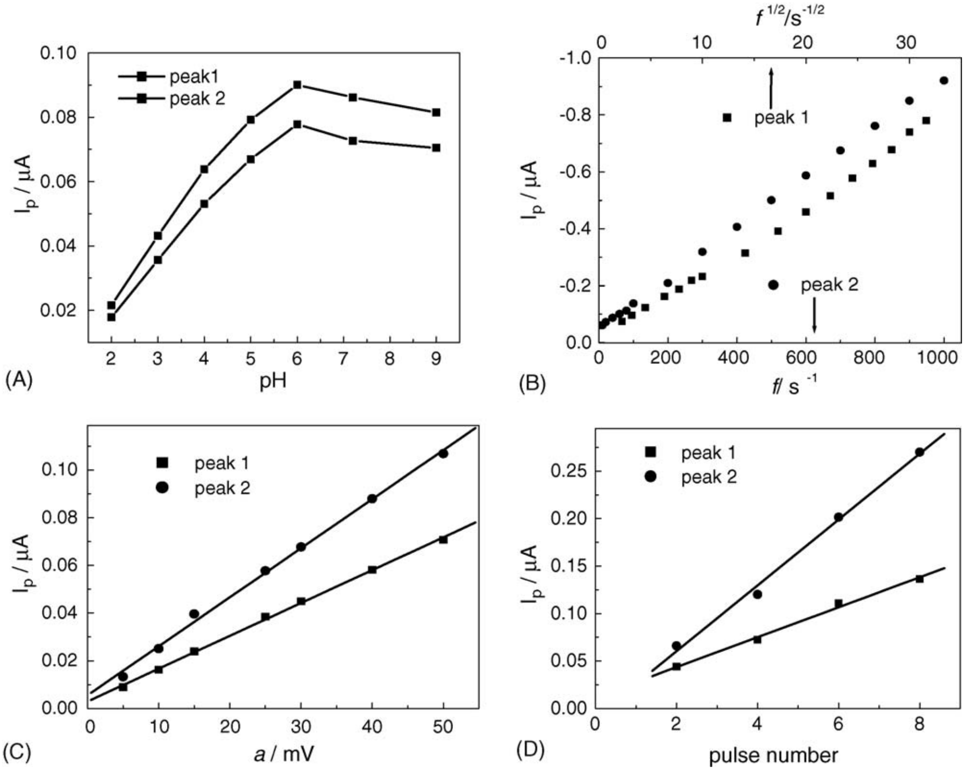

Fig. 2. Relationship between the peak current and pH (A), frequency of pulse potential (B) and pulse amplitude (C) obtained from square wave voltammograms of 5.0×10^{-5} mol L^{-1} paraquat in 0.10 mol L^{-1} Na_2SO_4 on Au-ME with variation of each parameters. Relationships between N and peak current for both peaks of reduction (D).

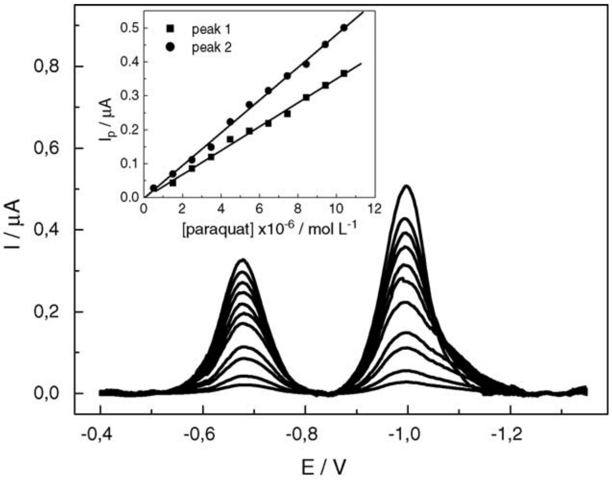

Fig. 3. Multiple square voltammograms for paraquat in $0.10\,\text{mol}\,\text{L}^{-1}$ Na_2SO_4 on Au-ME with $a = 50\,\text{mV}$, $\Delta E_s = 2\,\text{mV}$, $f = 250\,\text{s}^{-1}$ and different concentrations. Inset: analytical curves obtained considering the responses of peaks 1 and 2.

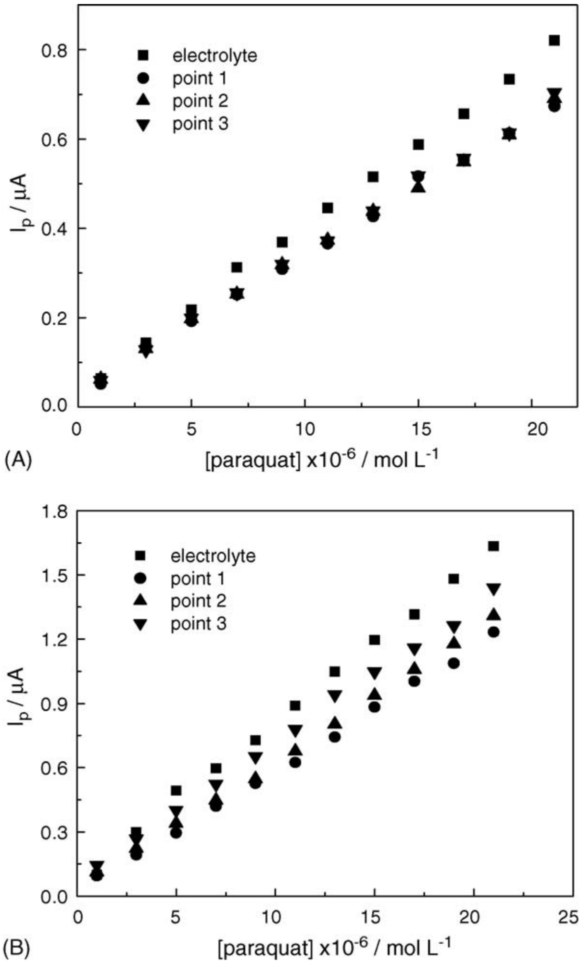

Fig. 4. Analytical curves obtained by MSWV for paraquat in electrolytes prepared with different natural waters samples, under the experimental conditions stated in Fig. 3 considering the responses of peak 1 (A) and peak 2 (B).

From the results presented in the table above, it can be observed that the values of DL and QL obtained for the support electrolyte prepared from Milli-Q water using the MSWV are shown to be of an order of magnitude of about 2 less than those obtained to those published in literature [20,31,32]. Such results are shown to be very appropriate for the determination of ultra-traces of paraquat in natural water, where the recommended maximum residue stipulated by the European Community [37] is 10 ppb, i.e., $10\,\mu\text{g}\,\text{L}^{-1}$.

The reproducibility of the method was determined by five successive measurements of the same $5.0 \times 10^{-6}\,\text{mol}\,\text{L}^{-1}$ of paraquat solution with a coefficient of variation of 1.8% and 2.0% for peaks 1 and peak 2, respectively, while the repeatability calculated at the same concentration level furnished a coefficient of variation of 1.2% and 1.98% for peak 1 and peak 2, respectively. These are indicative of the good precision and accuracy of the methodology and the possibility of its applications in complex samples.

3.4. Application to natural samples water

The suitability of the proposed methodology for the analysis of paraquat in complex samples was checked by determining a small concentration of paraquat pesticide in natural water samples artificially spiked. The analytical procedure earlier described in the preceding sections was applied for natural water samples collected in different points in Mogi-Guaçu river, as described in Section 2 of the present article. As mentioned before, the sampling points were selected based on the different levels of organic matter, including industrial and domestic pollution in the sampling points. The water samples were used as received, to prepare the support electrolyte (by adding $0.10\,\text{mol}\,\text{L}^{-1}$ Na_2SO_4) and corresponding analytical curves were again obtained applying for MSWV experiments. The analytical curves obtained under this new experimental condition are presented in Fig. 4 for both peak 1 and peak 2.

Table 1
Results obtained from linear regression curves (Fig. 3) for the determination of paraquat in pure electrolyte on Au-ME using MSWV

Parameter	Peak 1	Peak 2
Equation	$I(A) = -2.636 \times 10^{-9} + 3.525 \times 10^{-2}C$	$I(A) = -2.155 \times 10^{-9} + 4.822 \times 10^{-2}C$
r	0.9972	0.9985
S_b (A)	2.785×10^{-12}	3.124×10^{-11}
s (A/mol L^{-1})	3.525×10^{-2}	4.822×10^{-2}
DL (mol L^{-1})	2.370×10^{-10} (0.044 ppb)	1.944×10^{-9} (0.360 ppb)
QL (mol L^{-1})	7.901×10^{-10} (0.146 ppb)	6.479×10^{-9} (1.199 ppb)
Sensibility (nA/mol L^{-1})	3.525×10^{7}	4.822×10^{7}

Table 2
Results obtained from recovery curves of paraquat in natural water samples considering peak 1 and peak 2

Sample	Peak 1		Peak 2	
	[Rec.]×10^{-6}	% Rec.	[Rec.]×10^{-6}	% Rec.
Electrolyte	2.479	99.17	2.451	98.03
Point 1	2.292	91.71	2.064	82.67
Point 2	2.247	89.87	2.052	82.07
Point 3	2.02	80.48	1.972	78.88

Table 3
Results obtained from recovery curves of paraquat in food and beverages samples considering peak 1 and peak 2 on Au-ME and MSWV

Sample	Recovered concentration (×10^{-6} mol L^{-1})	Recovery (%)	R.S.D. (%)
Orange	2.214	88.59	1.89
Lemon	2.168	86.72	1.95
Apple	2.188	87.53	2.70
Potato	2.031	81.24	2.45
Sugar cane	2.272	85.46	3.90

The results that were obtained showed that I_p for peak 1 is practically not sensitive to the presence of the contaminants in natural samples. The analytic sensitivity, given as the slope of the analytical curves, is practically constant compared with those obtained from a pure water electrolyte, and hence does not dependent on the origin of the sample. This can be associated to the fact that the electrochemical process for peak 1 occurs for species in solution, being less sensitive to possible adsorption processes on the electrode surface. These values are shown to be very close to those published using the SWV traditional allied to Au-ME [20].

Recovery experiments were also carried out in order to evaluate the interference of matrix effects of the natural water samples on the reduction of paraquat on Au-ME. Recovery curves for the samples spiked with 2.495×10^{-6} mol L^{-1} paraquat were then obtained by the standard addition method. The results of the present study are shown in Table 2, for peaks 1 and 2. In all samples, the percentage recovered obtained for peak 1 and peak 2 presented satisfactory values for the proposed electroanalytical methods [35] thus indicating the suitability of the proposed method for use in natural water samples.

3.5. Application to food and beverages in natura

In Brazil, the paraquat is one of the most widely used herbicides in citric fruit, potato and apple cultures. Due to its permitted use in such cultures, the methodology proposed was applied in order to evaluate to occurrence of matrix effects in the electroanalytical determination of paraquat residues directly in the samples, without pre-treatment or clean up steps.

For the citric fruit samples, orange and lemon, the extract of the juices were extracted and had their pH values adjusted to 6.00 with an appropriate volume of 3.00 mol L^{-1} of NaOH solution. An aliquot of the 10 mL of each sample was added to the electrochemical cell for the posterior recovery experiments. The MSWV responses for electroanalytical reduction of paraquat directly in the samples demonstrated that peak 1 is free from interference. However, peak 2 overlays a background current, maybe related to other matrix components which, in the case of citric fruits, are basically ascorbic acid (Vitamin C) and citric acid.

This interference was also observed in previous work developed by De Souza and Machado [36]. The citric and ascorbic acids were added in the electrochemical cell containing the samples and paraquat. The MSWV responses were also evaluated and demonstrated that possible interference of citric and ascorbic acids exerts detectable effects on the recovery experiments only for peak 2, because the responses of the interferences occur at approximately −0.85 V. These values correspond to peak potential for peak 2 of the paraquat at Au-ME, indicating that in this peak value the adsorption process can be attributed to the adsorption of the matrix components at the electrode surface or to interactions between the pesticide molecule and components of the juice. For peak 1, the electrochemical process is related to electronic transfer without adsorption of the reagents or products; consequently, this peak does not present effects of matrix interference.

For apple and potato, 20 g of representative samples were transferred into an electrochemical cell, mixed and homogenized. The recovery studies were realized by adding an appropriate volume of paraquat standard solution (10^{-5} mol L^{-1}) to electrochemical cell. The recovery efficiency was calculated using Eq. (3), and the results obtained, in triplicate, were related to interference effects of the constituents of each sample. The results of relative standard deviations and recovery percentage that were obtained for peak 1, were considered satisfactory compared to those obtained using other analytical methods, considering that neither the extraction or preparation stages of the samples are necessary in the proposed methodology. The proposed methodology has therefore proven to be applicable for use in complex samples. For potato and apple samples the major interference was the starch and sucrose, respectively, due to the presence of these compounds in high concentration in the samples, but these interferences do not affect the analytical sensitivity for peak 1.

Considering the sugar cane samples, the major effects of matrix interference were observed due to the presence of some flavonoids and the higher concentration of sucrose in the constituents of the samples. However, the recovery percentages obtained for peak 1 is suitable for application in such samples.

Table 3 presents the recovery percentages and the relative standard deviation obtained for food and beverages samples using MSWV allied to Au-ME.

4. Conclusions

Two important conclusions can be drawn from this work. Firstly, even with a limited number of pulses in the same potential step, the MSWV represents an excellent alternative for the determination of ultra-traces of paraquat in pure electrolyte. The development of an instrumentation setup and software which applies more than 8 potential pulses in the same potential step would however permit the acquisition of more sensitive results, and consequently, the application of the proposed technique to even more complex samples. Secondly, the use of the ME makes the direct analysis of the samples possible without any necessity of pre-treatments or chemical preparation stages, the observed recovery percentage values were in a range (70–130%), which is considered very satisfactory for analytic applications.

In practice, the use of the multiple square wave voltammetry allied to gold microelectrodes makes possible the acquisition of the detection limits an order of magnitude of about 2 less than those published in literature. This sensitivity is much more convenient since, at this level, the analytical signal is proportional to the pulse number applied. Additionally, the proposed methodology was successfully applied in quantifying paraquat in natural water samples with very satisfactory recovery percentages values for the application of the analytic methods proposed. In fact, no such electroanalytical analysis of the pesticides residues using multiple square wave voltammetry has yet been reported.

Furthermore, this work demonstrates that frequent routine analyses can be safely carried out using simpler and less expensive electroanalytical methods without losses in either reliability or precision. The observed reproducibility and repeatability of the proposed methodology was below 2% for the two reduction peaks. These values are considered to very satisfactory, thus confirming the practicality of the proposed methodology.

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