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### Electrochemical study of butylate: application to the analysis of water

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## Electrochemical study of butylate: application to the analysis of water

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The electroactivity of butylate (BTL) is studied by cyclic voltammetry (CV) and square wave voltammetry (SWV) at a glassy carbon electrode (GCE) and a hanging mercury drop electrode (HMDE). Britton–Robinson buffer solutions of pH 1.9–11.5 are used as supporting electrolyte. CV voltammograms using GCE show a single anodic peak regarding the oxidation of BTL at +1.7 V *versus* AgCl/Ag, an irreversible process controlled by diffusion. Using a HMDE, a single cathodic peak is observed, at –1.0 V *versus* AgCl/Ag. The reduction of BTL is irreversible and controlled by adsorption. Mechanism proposals are presented for these redox transformations. Optimisation is carried out univariably. Linearity ranges were 0.10–0.50 mmol L<sup>-1</sup> and 2.0–9.0 μmol L<sup>-1</sup> for anodic and cathodic peaks, respectively. The proposed method is applied to the determination of BTL in waters. Analytical results compare well with those obtained by an HPLC method.

**Keywords:** butylate; voltammetry; glassy carbon electrode; hanging mercury drop electrode

### 1. Introduction

Butylate (BTL) is S-ethyl-di-isobutylthiocarbamate (Figure 1, structure I), a selective thiocarbamate herbicide extensively used to control grass weeds in corn [1,2], maize and pineapple [3]. Various biotic or abiotic factors influence the fate of pesticides in nature [4], though the peak of pesticide concentration is typically highest in late spring or early summer as it is associated with periods of runoff following application [5]. Environmental Protection Agency (EPA) indicates a Reference dose (RfD) for BTL of 0.05 mg kg<sup>-1</sup> per day. RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. The concentration of BTL in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to 1 or 10 days of exposure is 2 mg L<sup>-1</sup>, a value calculated for a 10 kg child consuming 1 L of water per day [6].

Although not classifiable as to human carcinogenicity, BTL has also a great potential for leaching into groundwater, although it is only slightly soluble in water [6]. It does not adsorb strongly to soil particles and is mostly mobile in soils [6–8]. When applied to dry soil surfaces, very little BTL is lost through vaporisation. However, it can be lost by

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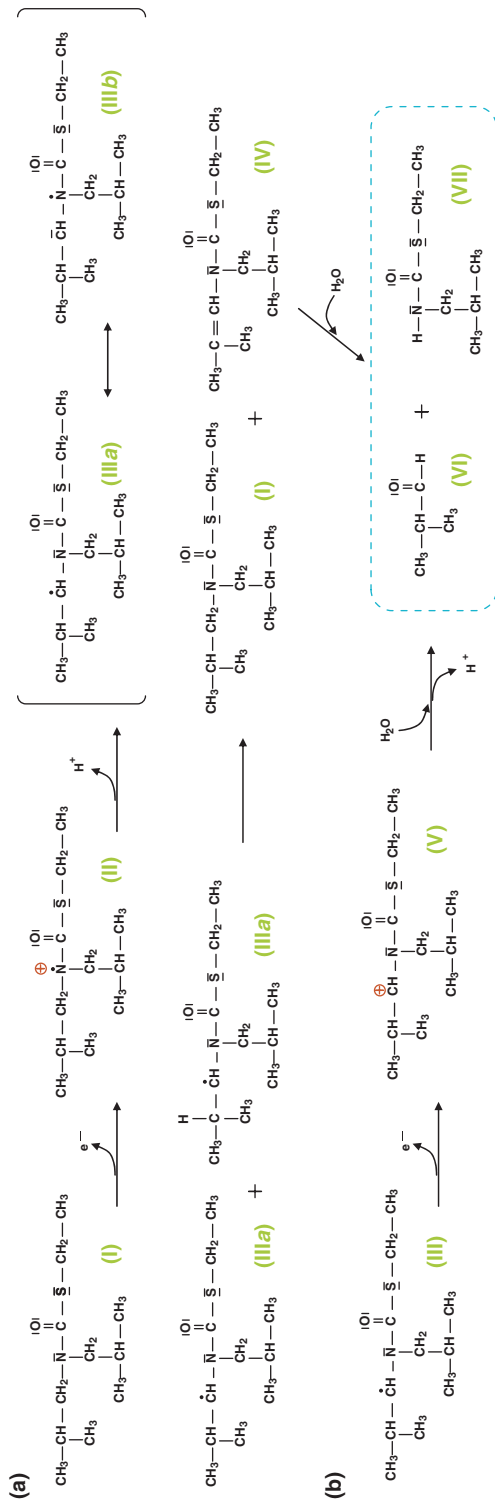


Figure 1. Electrochemical oxidation of BTL.

vaporisation when applied to the surface of wet soils [9,10]. Photodegradation by ultraviolet radiation from sunlight is one of the most powerful mechanisms of pesticide disappearance in water and air [11–13].

The great interest in BTL determination in environmental samples led to the development of several analytical methods mostly based on high-performance liquid chromatography (HPLC) and gas chromatography (GC). These techniques are associated to different kind of detectors, namely mass spectrometry (MS) [12–14], Flame ionisation detector (FID) [4,15] ultraviolet detection (UV) [16] and diode-array detection (DAD) [17]. These methods require time-consuming steps, such as extraction and/or adsorption techniques for sample clean-up, or derivation procedure for detection; they also use significant amounts of solvent and require sophisticated instrumentation.

Electrochemical methods have been widely applied to the determination of pesticides because they require reduced sample preparation and time-consuming extractions steps [18]. Few dithiocarbamate pesticides, such as thiram [19], zineb [20] and ziram [21] have been determined by mercury or carbon-based electrodes, showing linearity ranges within  $6 \times 10^{-6}$  to  $8 \times 10^{-5}$ , up to  $2 \times 10^{-6}$  mol L<sup>-1</sup>, and  $3 \times 10^{-8}$  to  $2 \times 10^{-6}$ , respectively. Some of the reported methods use adsorptive stripping strategies and allow the routine control of these pesticides in real samples.

Thus, the present article proposes electroanalytical procedures for the rapid analysis of BTL in environmental samples. The electrochemical behaviour and mechanism of BTL at a glassy carbon electrode (GCE) and a hanging mercury drop electrode (HMDE) are presented with regard to cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments.

## 2. Experimental

### 2.1 Reagents and solutions

BTL was purchased from Riedel-de-Haën and used without further purification. All other chemicals were Merck pro-analysis grade and all solutions were prepared using purified water (conductivity  $< 0.1 \mu\text{S cm}^{-1}$ ) obtained from a Barnstead E-pure 4 system.

A series of Britton–Robinson buffers (BR) ranging 1.9–11.5 pH was used as supporting electrolyte. It was prepared by mixing different volumes of phosphoric, acetic and boric acids stock solutions (containing each acid component at  $0.16 \text{ mol L}^{-1}$ ) and a  $0.80 \text{ mol L}^{-1}$  NaOH solution in order to obtain the required pH [22]. The ionic strength was adjusted to  $0.30 \text{ mol L}^{-1}$  by suitable dilution of a  $1.34 \text{ mol L}^{-1}$  KNO<sub>3</sub> solution with water.

Acetonitrile was HPLC grade (Merck, Germany). Prior to use, a binary solvent system (acetonitrile/water) was filtered and de-aerated by sonication.

### 2.2 Apparatus

All voltammetric measurements were performed with a computer controlled potentiostat/galvanostat Autolab PSTAT (EcoChemie, The Netherlands), and a Metrohm VA Stand containing a three-electrode cell (all Metrohm): GCE for the electrooxidation studies ( $\phi$  2.0 mm) or a HMDE for the reduction studies acting as working electrode, an Ag/AgCl/KCl  $3.00 \text{ mol L}^{-1}$  reference electrode and a glassy carbon rod counter electrode. The system was controlled by means of a General-Purpose Electrochemical System (GPES) software package, version 3.0, from Ecochemie.

A pH meter (Metrohm E-520) with a combined glass electrode (Crison CWL/S7) was used for pH measurement.

GCE were mechanically cleaned before each experiment by polishing its surface in a polishing kit (Metrohm 6.2802.010), first with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0.3  $\mu$ m) until a shining surface was obtained and after with purified water. After polishing, the electrode was thoroughly washed and dried with tissue paper. Less aggressive cleaning procedures may be applied, such as soaking in organic solvents for 1–2 min and cleaning afterwards using a paper soaked in water for 0.5–1 min, but these were not tried out.

Chromatographic separations were carried out in a Shimadzu liquid chromatograph system with UV-vis DAD, configured to detect at 190 nm. The injector was a Rheodyne Model 77251i (Cotati, CA, USA), fitted with a 20  $\mu$ L external loop. The analytical column was a Waters Spherisorb<sup>®</sup> (4.6  $\times$  250 mm<sup>2</sup> i.d.; 5  $\mu$ m particle size). Data acquisition was carried out by LcSolution software.

### 2.3 Standard and sample preparations

A standard stock solution of BTL (10.0 mmol L<sup>-1</sup>) was prepared by dissolving an accurately weighed amount of the pure pesticide in acetonitrile, and completing to final volume with water. Only a few drops of acetonitrile were used to enhance the dissolution of the solid pesticide. Standard solutions were prepared by dilution of this stock solution with water and were stable for at least 1 week, when stored in the dark at 4°C.

Natural water samples were collected from various locations in Porto, Portugal (rivers and lakes), in dark glass bottles to prevent light alterations. The samples were spiked with BTL and directly analysed by electrochemical and chromatographic techniques using the calibration curve method. No acetonitrile was added to the samples.

### 2.4 Method comparison

Results from voltammetric analysis were compared with those obtained using HPLC with UV-vis DAD. HPLC was performed at room temperature with water and acetonitrile (20 : 80 v/v) as mobile phase at flow rate of 0.6 mL min<sup>-1</sup>. The retention time for BTL was 12.8 min. Calibration was performed by injection of 20  $\mu$ L of BTL standard solutions ranging 2.0–9.0  $\mu$ mol L<sup>-1</sup>.

### 2.5 Analytical procedures

All electrochemical measurements were conducted in aqueous media. The anodic behaviour of BTL was studied at a GCE. CV and SWV experiments were carried out in BR buffer solutions of 0.3 mol L<sup>-1</sup> ionic strength and varying pHs (1.9–11.5). The electrodes were immersed in 10.0 mL of buffer at the electrochemical cell, and a stream of pure nitrogen was purged through it to ensure oxygen removal. The scan was initiated in the positive direction of the applied potential from 1.30 to 1.90 V. After recording the voltammogram of the buffer solution, an accurate volume of the pesticide solution (500  $\mu$ L) was added. A 30-s period for purging nitrogen was allowed before recording the voltammogram of each test solution. Voltammetric trials were conducted under different operating conditions of pH, frequency, scan rate and pulse amplitude. Before each measurement the GCE was manually polished as previously described.

Cathodic studies were carried out with a HMDE. Similarly to GCE-based studies, BTL standard solutions were prepared in BR buffer of different pHs (1.9 to 11.5), and CV and SWV techniques were used. After recording the voltammogram of the blank, a known volume of the BTL stock solution ( $10.0 \text{ mmol L}^{-1}$ ) was added to  $10.0 \text{ mL}$  of BR buffer in the electrochemical cell. The final solution was deoxygenated with purified nitrogen for 10 min in the first cycle and for 30 s for each successive cycle. In this case, the electrode surface is automatically renewed each scan for which no cleaning procedures were required. Voltammograms were scanned from  $-0.50$  to  $-1.30 \text{ V}$ .

### 3. Results and discussion

#### 3.1 Electrooxidation of butylate with GCE

##### 3.1.1 Preliminary evaluations

CV preliminary studies were made to elucidate the electrochemical oxidation of BTL. Voltammograms within  $1.30$ – $1.90 \text{ V}$  (vs.  $\text{AgCl/Ag}$ ) showed a single anodic peak at about  $+1.7 \text{ V}$  (Figure 2, CV). The potential of this peak ( $E_p$ ) was independent from pH. No cathodic peak was observed in the reverse scan, indicating the irreversible nature of the electrochemical oxidation of BTL within the investigated potential window [23].

##### 3.1.2 Effect of scan rate

The influence of the scan rate ( $\nu$ ) ranging  $10$ – $200 \text{ mV s}^{-1}$  on the peak current ( $i_p$ ) was evaluated at pH 4.4. Increasing scan rates produced a linear relationship between the peak current and the square root of the scan rate (Figure 2, CV), following the equation ( $i_p (\mu\text{A}) = 0.52 \nu^{1/2} (\text{mV s}^{-1})^{1/2} + 0.06$ ;  $r = 0.994$ ). This indicated that BTL oxidation at the electrode surface was mainly controlled by diffusion [23].

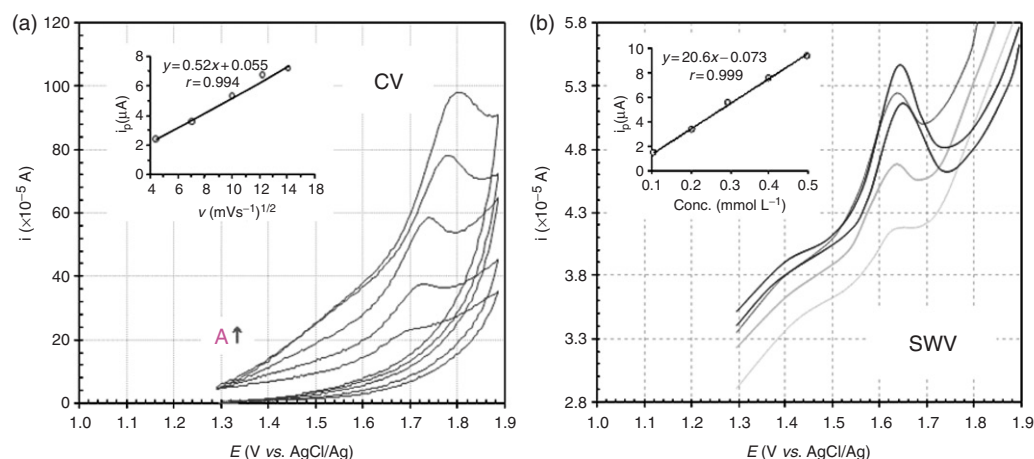


Figure 2. Oxidation of BTL at a GCE dipped in a pH 4.43 BR buffer. Cyclic voltammograms of  $5.0 \times 10^{-2} \mu\text{mol L}^{-1}$  BTL standard solution for increasing scan rate ( $A \uparrow$ ) ranging  $20$ – $200 \text{ mV s}^{-1}$ ; inset is linear relationship between the peak current and the square root of the scan rate. Square wave voltammograms of BTL standard solutions ( $f = 50 \text{ Hz}$ ); inset is the corresponding calibration curve.

### 3.1.3 Number of electrons and diffusion coefficient

The number of electrons and the diffusion coefficient value were determined by the application of Randle and Sevcik mathematical equation [23] (Equation (1)), where  $i_p$  (BTL),  $i_p$  (Fe) are peak current (A);  $n_{(\text{BTL})}$ ,  $n_{(\text{Fe})}$  are number of electrons;  $A$  is the surface area of the electrode ( $\text{cm}^2$ );  $\alpha n_\alpha$  is the electrochemical transfer coefficient;  $D_{(\text{BTL})}$  and  $D_{(\text{Fe})}$  are diffusion coefficients ( $\text{cm}^2 \text{s}^{-1}$ );  $C_{(\text{BTL})}$  and  $C_{(\text{Fe})}$  are the same concentrations ( $\text{mol L}^{-1}$ ) in the same solvent, of BTL and Fe, and  $\nu$  scan rate ( $\text{V s}^{-1}$ ) of BTL and Fe, respectively.

The electrochemical transfer coefficient,  $\alpha n_\alpha$  was calculated by application of Equation (2), where  $\alpha$  is transfer coefficient,  $n_\alpha$  is the number of electrons involved till rate limiting step, and  $E_{p1/2}$  is the potential in Volts that corresponds to  $i_{p1/2}$ .

Considering that the reduction of hexacyanoferrate (III) involved one electron *per* molecule [23], the Randles-Sevcik equation indicated that the oxidation of BTL involved  $2.0 \pm 0.3$  electrons *per* molecule and the diffusion coefficient was  $1.5 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$ .

$$\frac{i_p(\text{BTL})}{i_p(\text{Fe})} = \frac{2.99 \times 10^5 n_{(\text{BTL})} (\alpha n_\alpha) A D_{(\text{BTL})} C_{(\text{BTL})} \nu^{1/2}}{2.69 \times 10^5 n_{(\text{Fe})}^{3/2} A D_{(\text{Fe})} C_{(\text{Fe})} \nu^{1/2}} \quad (1)$$

$$E_p - E_{p/2} = \frac{0.048}{\alpha n_\alpha} \quad (2)$$

### 3.1.4 Mechanistic considerations

The observed anodic peak corresponded to the loss of two electrons from BTL. Most probably, these electrons are derived from the oxidation of the nitrogen atom (Figure 1). This oxidation is typically carried out at high potentials [24] and involves the formation of highly unstable intermediates. For BTL, the oxidation of the nitrogen atom is expected to produce a radical cation radical (Figure 1, structure II) that deprotonates to give a neutral species. The single electron may be stabilised by charge delocalisation [24] produced by resonance structures with unpaired electrons (Figure 1, structures IIIa and IIIb). Then, two paths are opened for this either a dismutation to an ‘amine’ and ‘enamine’ (Figure 1, path A) or an oxidation to a ‘minimum’ cation (Figure 1, path B). In both ways, the overall reaction provides an amine, an aldehyde and protons [24]. Further studies should be conducted to confirm this mechanism proposal in organic medium. This mechanism is a mere proposal and further studies should be conducted to confirm it in organic and aqueous medium.

### 3.1.5 pH effect

Influence of pH on BTL peak shape and peak height was carried out in SWV, a more sensitive and rapid technique than other electrochemical approach. This study was done using a  $0.50 \text{mmol L}^{-1}$  BTL solution and BR buffers over a wide pH range (1.9 to 11.5). The electrochemical activity of BTL started at pH 2.5. The anodic peak was at +1.65 V *versus* AgCl/Ag and maximum peak currents were at pH 4.4. No significant variations were observed in peak potential ( $E_p$ ) within this range.

### 3.1.6 Analytical features

Calibration curves of BTL solutions of pH 4.4 showed linear behaviour within  $0.10\text{--}0.50 \text{mmol L}^{-1}$  (Figure 2, SWV) according to the following equation:  $[i_p(\mu\text{A}) =$



$20.60 \pm 0.02$  ( $\mu\text{mol L}^{-1}$ )  $- 0.73 \pm 0.03$ ;  $r = 0.999$ ]. Each point of calibration curve is the mean value of four independent measurements. Limit of detection (LOD) and limit of quantification (LOQ) were obtained after the equations  $\text{LOD} = 3\sigma/s$  and  $\text{LOQ} = 10\sigma/s$ , where  $\sigma$  is standard deviation of the intercept and  $s$  slope of the calibration plot [25]. The calculated LOD value of BTL was  $4.96 \mu\text{mol L}^{-1}$  and the LOQ value  $16.5 \mu\text{mol L}^{-1}$  (Table 1).

### 3.2 Electroreduction of butylate with HMDE

When mercury is used as working electrode lower detection limits are expected. This is an important issue to detect/quantify pesticides on environmental samples. However, the use of mercury is restricted because of its toxicity to living beings and for being an environmental hazard. Thus, specific procedures were conducted to establish an HDME-based method. Mercury dropped in working solutions was selectively collected and followed suitable recovery procedures. This strategy ensured both economical and environmental benefits.

#### 3.2.1 Preliminary experiments

Cyclic voltammograms of  $10.0 \mu\text{mol L}^{-1}$  BTL show a single and well-defined cathodic peak at about  $-1.0 \text{ V}$  versus AgCl/Ag (Figure 4, CV). This electrochemical reaction was of irreversible nature. The current of the cathodic peak current was directly proportional to the scan rate, over the range  $20\text{--}300 \text{ mV s}^{-1}$  following the equation, ( $i_p (\times 10^{-2} \mu\text{A}) = 3.77 \times 10^{-2} v (\text{mV s}^{-1}) + 3.78 \times 10^{-1}$ ;  $r = 0.994$ ); this is expected for a mass transport process controlled by adsorption.

#### 3.2.2 Mechanistic considerations

According to literature, results suggest that the reducible unit in BTL could be the sulfur atom [26]. This is consistent with a peak potential of about  $-1.0 \text{ V}$ . Another possibility could be the reduction of the carbonyl function to a hydroxyl group. However, the potential of this transformation is pH dependent, which is inconsistent with the observed behaviour.

Table 1. Main analytical features of voltammetric calibration curves of Cys using GCE and HMDE ( $n = 4$ ) and HPLC technique ( $n = 3$ ).

| Parameter   | GCE                              | HMDE                             | HPLC                             |
|---|----------------------------------|----------------------------------|----------------------------------|
| Range concentration ( $\mu\text{mol L}^{-1}$ )                    | 10.0–50.0                        | 2.00–9.00                        | 2.00–9.00                        |
| Slope ( $\text{A mol}^{-1} \text{ dm}^{-3}$ )                     | $(20.6 \pm 0.02) \times 10^{-4}$ | $(0.89 \pm 0.03) \times 10^{-4}$ | $(1.69 \pm 0.04) \times 10^{10}$ |
| Intercept (A)   | $(0.73 \pm 0.03) \times 10^{-6}$ | $(0.68 \pm 0.08) \times 10^{-8}$ | $(5.80 \pm 0.09) \times 10^3$    |
| Correlation coefficient ( $n = 10$ )                              | 0.999                            | 0.995                            | 0.999                            |
| LOD ( $\mu\text{mol L}^{-1}$ )                                    | 4.96                             | 0.29                             | 0.10                             |
| IUPAC<br>( $3 \times S_{\text{standard deviation blank/slope}}$ ) | 16                               | 1.64                             | 0.53                             |
| Clayton criterion   | 16                               | 1.64                             | 0.53                             |
| LOQ ( $\mu\text{mol L}^{-1}$ )                                    | 16.5                             | 0.96                             | 0.34                             |



### 3.2.3 Electrochemical and chemical variables

In search of higher currents and well-defined peaks, several parameters of chemical (pH) and electrochemical (frequency ( $f$ ), deposition potential ( $p_d$ ), deposition time ( $t_d$ ), step potential and pulse amplitude) nature were optimised. Figure 3 shows the effect of these voltammetric variables in the peak current. This optimisation was performed unvaryingly.

The influence of pH on the reduction of  $10.0 \mu\text{mol L}^{-1}$  BTL was investigated using BR buffer over the pH range 1.9–11.5. No electroactivity was found for  $\text{pH} < 3.3$ . Voltammograms showed always a single cathodic peak at  $-1.0 \text{ V}$  (vs.  $\text{AgCl/Ag}$ ) for higher pHs. Maximum peak currents were recorded in the acidic range where no significant variations were observed in  $E_p$ . The frequency was varied from 10 to 200 Hz. Values of  $i_p$  increased with the frequency until 50 Hz; above this value peaks became distorted. The dependence of  $i_p$  on  $p_d$  was studied in the range  $-0.40$  to  $-0.70 \text{ V}$  versus  $\text{AgCl/Ag}$ . Deposition potentials above  $-0.50 \text{ V}$  ensured high peak current. The effect of  $t_d$  on the preconcentration was also evaluated, for 0–200 s. Values of  $i_p$  were at its maximum at 5 s of accumulation; above this value a decrease in peak definition was observed. Step potentials were varied within 1–8 mV. Peak currents ( $i_p$ ) increased linearly with step, up to 4 mV. Above this value  $i_p$  values decreased. Pulse amplitude was evaluated from 10 to 50 mV

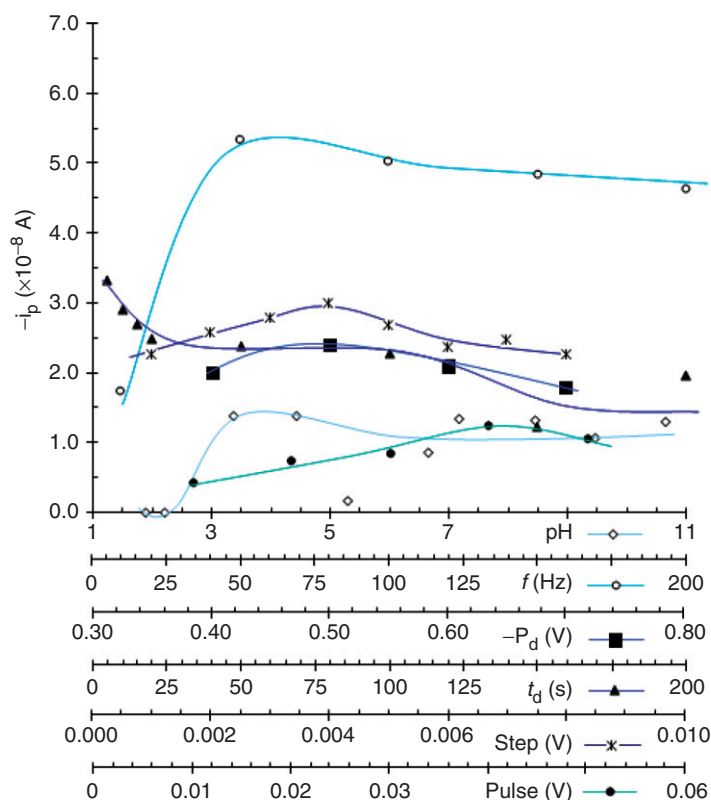


Figure 3. Univariable optimisation of several voltammetric variables (pH,  $f$ ,  $p_d$ ,  $t_d$ , step and pulse) in the analytical signal of  $10.0 \mu\text{mol L}^{-1}$  BTL solution at HMDE. Different experimental conditions in each variable under study are indicated in the X-axis.

presenting a maximum activity at 40 mV. The SWV optimal conditions selected after the previous studies were pH = 3.3,  $f = 50$  Hz,  $p_d = 0.5$  V,  $t_d = 5$  s, step potential = 4 mV and pulse amplitude = 40 mV.

### 3.2.4 Analytical features

Table 1 presents the calibration data obtained using the optimised conditions. Linear behaviour was observed from 2.0 to 9.0  $\mu\text{mol L}^{-1}$ , with a linear equation of ( $i_p \times 10^{-2} \mu\text{A}$ ) =  $0.89 \pm 0.03$  ( $\mu\text{mol L}^{-1}$ ) +  $0.68 \pm 0.08$ ;  $r = 0.995$ ) (Figure 4). Each point of the calibration curve was the mean value of four independent measurements.

The LOD and LOQ were calculated from the linear calibration plot [25] and the Clayton criteria [27]. Generally, the LOD for HMDE method was more than 10 times below the ones observed for the GCE. This higher detection capability of mercury electrode was already expected and points out the possibility of its application to the analysis of environmental water samples.

The precision of the HMDE method was investigated by intra-day and inter-day determination of BTL at two different concentrations and was determined by calculating relative standard deviations (Table 2). For intra-day studies each concentration was assessed by performing 10 repeated measurements for three times along each working day. For inter-day measurements studies were performed over a period of 1 week. No significant differences were found between intra-day and inter-day experiments. RSD values ranged 1.56–4.30%, indicating the high precision of the voltammetric readings.

The accuracy was determined by calculating percentage relative errors (RE%) between measured and added concentrations. Results obtained are indicated in Table 2. RE are always < 5% and the percentage of recoveries (R%) ranged 99.0–105%, confirming the accuracy of the method.

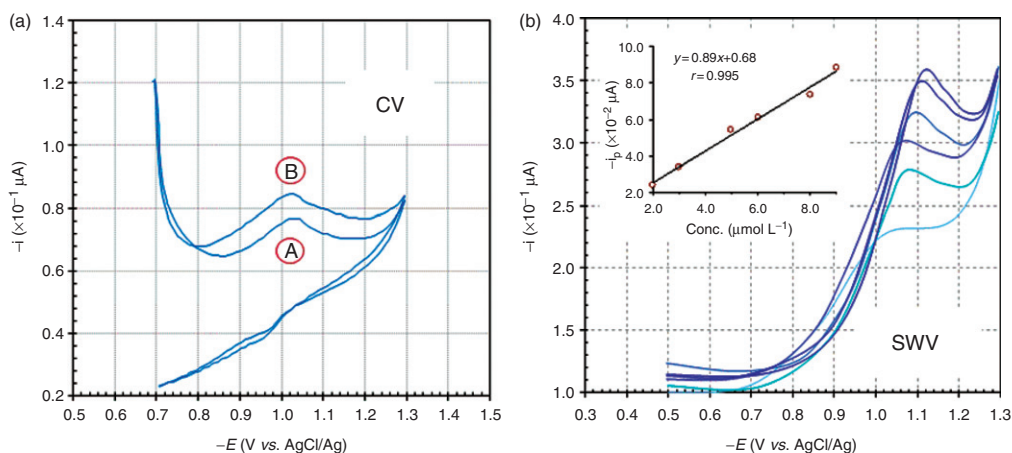


Figure 4. Reduction of BTL by a HMDE in a BR buffer of pH 3.3. Cyclic voltammograms of 10  $\mu\text{mol L}^{-1}$  BTL standard and different scan rates ((a) 100  $\text{mV s}^{-1}$  and (b) 150  $\text{mV s}^{-1}$ ). Square wave voltammograms of BTL standard solutions (pH 3.3;  $f = 50$  Hz,  $p_d = -0.50$  V;  $t_d = 5$  s) of increasing concentrations (2.0; 3.0; 5.0; 6.0; 8.0; 9.0  $\mu\text{mol L}^{-1}$ ); inset is corresponding calibration curve.

Table 2. Analytical precision and accuracy of assay of BTL using SWV technique in HMDE.

| Concentration<br>( $\times 10^{-6}$ mol L $^{-1}$ ) | Intra-day <sup>a</sup>              |          |           |            | Inter-day <sup>b</sup>              |          |           |            |
|---|-------------------------------------|----------|-----------|------------|-------------------------------------|----------|-----------|------------|
|   | Found<br>( $\mu\text{mol L}^{-1}$ ) | R<br>(%) | RE<br>(%) | RSD<br>(%) | Found<br>( $\mu\text{mol L}^{-1}$ ) | R<br>(%) | RE<br>(%) | RSD<br>(%) |
| 5.00  | 5.10                                | 102      | +2.00     | 2.38       | 5.25                                | 105      | +5.00     | 1.56       |
| 7.80  | 7.72                                | 99.0     | -1.03     | 4.30       | 7.90                                | 101      | +1.28     | 1.77       |

<sup>a</sup>Average of 10 measurements three times along a day; <sup>b</sup>Average of 10 measurements over a week; R: recovery; RE: relative error; RSD: relative standard deviation.

R (%) =  $[\text{BTL}]_{\text{found}}/[\text{BTL}]_{\text{added}} \times 100$ .

RE (%) =  $([\text{BTL}]_{\text{found}} - [\text{BTL}]_{\text{added}})/[\text{BTL}]_{\text{added}} \times 100$ .

RSD (%) = standard deviation/[BTL] mean found  $\times 100$ .

To assess the possible chemical degradation of BTL in aqueous media, the  $i_p$  value of  $5.0 \mu\text{mol L}^{-1}$  BTL solution was measured along the same day. No significant changes were observed in peak currents and peak potentials.

### 3.3 Selectivity studies

The effect of foreign organic and inorganic species on the electrochemical readings was examined by adding different amount of other species to a solution containing  $5.0 \times 10^{-6}$  mol L $^{-1}$  BTL. The tolerance limit was fixed as the maximum amount containing an error in peak current  $\leq 7\%$ .

As organic species, other pesticides and humic acids were tested (Table 3). Different tolerance levels were found for these: molinate ( $1 \mu\text{mol L}^{-1}$ ), bentazone (up to  $50 \mu\text{mol L}^{-1}$ ), MCPA ( $5 \mu\text{mol L}^{-1}$ ), propanyl ( $0.1 \mu\text{mol L}^{-1}$ ) and humic acid ( $2.5 \text{ mg L}^{-1}$ ). With regard to pesticides, their interference may be considered negligible. Propanyl is the one playing the highest interference but its association to field application of BTL is highly improbable.

The effect of calcium, magnesium and other metal contaminants of water was also assessed (Table 4). Lead, calcium, iron, copper and manganese are tolerated up to  $50 \mu\text{mol L}^{-1}$ . Aluminum and silicon had tolerance levels of 25 and  $5 \mu\text{mol L}^{-1}$ . Other metals such as arsenium, cobalt and selenium caused serious positive interference because of their reduction under the experimental conditions. Their tolerance levels were  $0.1 \mu\text{mol L}^{-1}$ . Separation of BTL from zinc and chromium interfering species by solvent extraction and/or an ion-exchange procedure are necessary to avoid interference when large amount of these ions co-exist in the sample.

### 3.4 Analytical applications

SWV with HMDE was applied to the analysis of spiked water samples. The calibration method was used to analyse samples by three independent measurements. The results are given in Table 5.

The quality of the analytical results was assessed by determining BTL by an HPLC UV-vis DAD method. Figure 5 depicts typical chromatograms of a BTL standard solution and spiked sample. Table 1 summarises concentration ranges and other calibration figures of merit, as well as the LOD and LOQ for the HPLC method.

Table 3. Interfering effect of other pesticides and humic acid at BTL readings by HDME (peak currents obtained of BTL  $5.0 \times 10^{-6}$  mol L<sup>-1</sup> standard solutions prepared without or with a possible interfering compound at different ratios and the corresponding relative error).

| Interfering specie (Isp) |           | $-i_p$ ( $\times 10^{-8}$ A) |                 | Relative error (%) |
|--------------------------|-----------|------------------------------|-----------------|--------------------|
| Compound                 | BTL : Isp | Without                      | With            |                    |
| Molinate                 | 10 : 1    | $0.79 \pm 0.01$              | $0.78 \pm 0.06$ | -0.50              |
|                          | 5 : 1     |                              | $0.81 \pm 0.02$ | +2.53              |
|                          | 1 : 1     |                              | $2.52 \pm 0.05$ | +68.7              |
|                          | 1 : 5     |                              | $13.9 \pm 0.23$ | +1659              |
|                          | 1 : 10    |                              | $125 \pm 0.04$  | +15722             |
| Bentazone                | 10 : 1    | $2.22 \pm 0.09$              | $2.15 \pm 0.02$ | -3.15              |
|                          | 5 : 1     |                              | $2.10 \pm 0.04$ | -5.21              |
|                          | 1 : 1     |                              | $2.30 \pm 0.06$ | +3.60              |
|                          | 1 : 5     |                              | $2.37 \pm 0.03$ | +6.76              |
|                          | 1 : 10    |                              | $2.13 \pm 0.08$ | -4.05              |
| MCPA                     | 10 : 1    | $1.19 \pm 0.05$              | $1.17 \pm 0.10$ | -1.68              |
|                          | 5 : 1     |                              | $1.10 \pm 0.06$ | -7.56              |
|                          | 1 : 1     |                              | $1.20 \pm 0.03$ | +0.84              |
|                          | 1 : 5     |                              | $0.76 \pm 0.04$ | -36.1              |
|                          | 1 : 10    |                              | $0.74 \pm 0.06$ | -37.8              |
| Propanyl                 | 10 : 1    | $1.72 \pm 0.02$              | $1.69 \pm 0.02$ | -1.74              |
|                          | 5 : 1     |                              | $3.69 \pm 0.04$ | +114.6             |
|                          | 1 : 1     |                              | Without peak    |                    |
|                          | 1 : 5     |                              |                 |                    |
|                          | 1 : 10    |                              |                 |                    |
| Humic acid               | 10 : 1    | $4.13 \pm 0.05$              | $4.20 \pm 0.07$ | +1.69              |
|                          | 5 : 1     |                              | $4.29 \pm 0.05$ | +3.87              |
|                          | 1 : 1     |                              | $4.00 \pm 0.01$ | -3.15              |
|                          | 1 : 2.5   |                              | $4.12 \pm 0.02$ | -0.24              |
|                          | 1 : 5     |                              | $2.12 \pm 0.01$ | -48.67             |
|                          | 1 : 10    |                              | $1.16 \pm 0.03$ | -71.91             |

Relative errors were always <5% and the recovery trials ranged from 96 to 101%. Statistical analysis based on student's *t*-test showed no significant differences between electrochemical and comparison methods. For a confidence interval of 95%, the calculated *t* was lower than the critical one, thus confirming the accuracy of the proposed methods.

The proposed methods provide economical and environmental advantages, when compared to the HPLC method. The volume of wastes *per* analysis was about 10 mL for the electrochemical approach given that all standard solutions were prepared in the electrochemical cell, whereas large volumes of mobile phases were needed for LC analysis.

#### 4. Conclusion

The electrooxidation of BTL is an irreversible process controlled by diffusion with a transfer of two electrons per molecule. The cathodic reduction is irreversible and adsorption controlled.

Table 4. Interfering effect from inorganic compounds at BTL readings by HDME (see conditions in Table 3).

| Interfering specie (Isp) |           | $-i_p (\times 10^{-8} \text{ A})$ |                 |                    |
|--------------------------|-----------|-----------------------------------|-----------------|--------------------|
| Compound                 | BTL : Isp | Without                           | With            | Relative error (%) |
| Lead                     | 10 : 1    | $3.75 \pm 0.03$                   | $3.62 \pm 0.02$ | -3.47              |
|                          | 5 : 1     |                                   | $3.70 \pm 0.02$ | -1.33              |
|                          | 1 : 1     |                                   | $3.59 \pm 0.04$ | -4.27              |
|                          | 1 : 5     |                                   | $3.58 \pm 0.05$ | -4.53              |
|                          | 1 : 10    |                                   | $3.79 \pm 0.04$ | +1.07              |
| Calcium                  | 10 : 1    | $3.30 \pm 0.08$                   | $3.18 \pm 0.01$ | -3.64              |
|                          | 5 : 1     |                                   | $3.35 \pm 0.09$ | +1.52              |
|                          | 1 : 1     |                                   | $3.20 \pm 0.03$ | -3.03              |
|                          | 1 : 5     |                                   | $3.46 \pm 0.04$ | +4.85              |
|                          | 1 : 10    |                                   | $3.40 \pm 0.03$ | +3.03              |
| Iron                     | 10 : 1    | $3.00 \pm 0.03$                   | $3.07 \pm 0.01$ | +2.33              |
|                          | 5 : 1     |                                   | $2.90 \pm 0.05$ | -3.33              |
|                          | 1 : 1     |                                   | $2.86 \pm 0.02$ | -4.67              |
|                          | 1 : 5     |                                   | $3.15 \pm 0.05$ | +5.00              |
|                          | 1 : 10    |                                   | $3.06 \pm 0.03$ | +2.99              |
| Manganese                | 10 : 1    | $3.06 \pm 0.04$                   | $2.96 \pm 0.05$ | -3.27              |
|                          | 5 : 1     |                                   | $3.20 \pm 0.03$ | +4.58              |
|                          | 1 : 1     |                                   | $2.99 \pm 0.06$ | -2.29              |
|                          | 1 : 5     |                                   | $3.07 \pm 0.07$ | +0.33              |
|                          | 1 : 10    |                                   | $3.11 \pm 0.04$ | +1.63              |
| Copper                   | 10 : 1    | $3.10 \pm 0.06$                   | $3.13 \pm 0.02$ | +0.96              |
|                          | 5 : 1     |                                   | $3.20 \pm 0.01$ | +3.23              |
|                          | 1 : 1     |                                   | $3.00 \pm 0.04$ | -3.23              |
|                          | 5 : 1     |                                   | $2.93 \pm 0.05$ | -5.48              |
|                          | 1 : 10    |                                   | $3.06 \pm 0.03$ | -1.29              |
| Aluminum                 | 10 : 1    | $4.01 \pm 0.05$                   | $4.20 \pm 0.03$ | +4.74              |
|                          | 5 : 1     |                                   | $4.15 \pm 0.01$ | +3.49              |
|                          | 1 : 1     |                                   | $3.86 \pm 0.07$ | -3.74              |
|                          | 1 : 5     |                                   | $3.80 \pm 0.08$ | -5.24              |
|                          | 1 : 10    |                                   | $2.40 \pm 0.04$ | -67.08             |
| Silicon                  | 10 : 1    | $3.27 \pm 0.08$                   | $3.08 \pm 0.05$ | -3.75              |
|                          | 5 : 1     |                                   | $2.96 \pm 0.07$ | -9.48              |
|                          | 1 : 1     |                                   | $2.85 \pm 0.05$ | -12.84             |
|                          | 1 : 5     |                                   | $1.06 \pm 0.03$ | -66.88             |
|                          | 1 : 10    |                                   | Without peak    |                    |

Table 5. Determination of BTL in spiked water by voltammetric method, SWV at HMDE and by the comparison method, HPLC-UV/vis diode array detector.

| Sample | SWV-HMDE<br>( $\mu\text{mol L}^{-1}$ ) | HPLC<br>( $\mu\text{mol L}^{-1}$ ) | R (%) | RE (%) |
|--------|--|------------------------------------|-------|--------|
| 1      | $7.13 \pm 0.05$                        | $7.06 \pm 0.03$                    | 99.0  | +0.92  |
| 2      | $7.80 \pm 0.02$                        | $7.90 \pm 0.04$                    | 101   | -1.26  |
| 3      | $8.48 \pm 0.04$                        | $8.22 \pm 0.06$                    | 96.9  | +3.16  |

Mean and standard deviation from three determinations by HMDE and HPLC. R: recovery; RE: relative error.

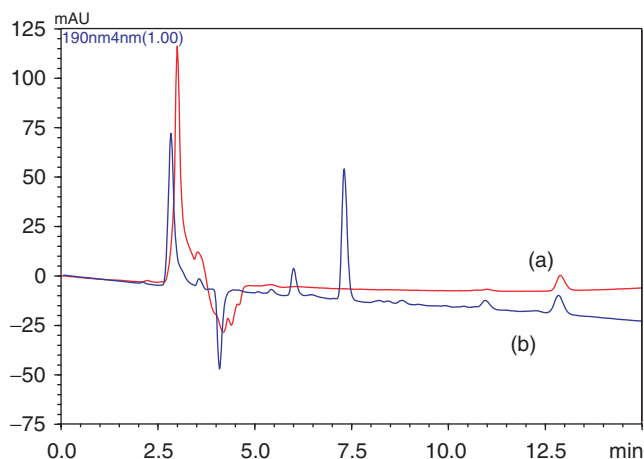


Figure 5. Liquid chromatograms from the analysis of (a)  $7.0 \mu\text{mol L}^{-1}$  standard solution of BTL and (b) spiked water with the same concentration.

A SWV procedure is developed to quantify BTL in water samples. The proposed method is a good alternative to others described in literature, and suitable to a routine environmental control of waters. LOD and LOQ values are near those reported in literature for HPLC-UV assays [16]. No previous sample treating steps were required prior to analysis, and the complete analysis took about 2 min. It offers fast analysis, low cost, and applicability over a wide range of concentrations, with minimal sample pre-treatment. For routine application economical and environmental benefits outcome from the low toxicity and volume of emitted effluents.

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