Electrochemical Study of Flumetralin with a Cyclic Renewable Silver Amalgam Film Electrode

Dariusz Guziejewski [a], Sylwia Smarzewska [a], Agnieszka Nosal-Wiercińska [b], and Radovan Metelka [c]

[a] University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, 92-236 Łódź, Poland, E-mail: dguziejewski@uni.lodz.pl

[b] Maria Curie-Sklodowska University, Faculty of Chemistry, Department of Analytical Chemistry and Instrumental Analysis, 20-031 Lublin, Poland.

[c] University of Pardubice, Faculty of Chemical Technology, Department of Analytical Chemistry, 53210 Pardubice, Czech Republic, E-mail: radovan.metelka@upce.cz

Abstract

The electrochemical properties of flumetralin (FLM) were investigated using square wave stripping voltammetry (SWSV) at cyclic renewable silver amalgam film electrode (Hg(Ag)FE). Two cathodic signals of FLM were recorded at Hg(Ag)FE in Britton-Robinson buffer of pH 9.5. After optimization of SWSV parameters and pH of supporting electrolyte, the linearity of peak currents vs concentrations of FLM was found in the range of 5×10^{-7} mol L^{-1} - 1×10^{-5} mol L^{-1} with a detection limit 6.43×10^{-08} mol L^{-1}. The developed method has been applied for the quantitative analysis of FLM in spiked tap water.

Key words: Flumetralin determination, Square wave voltammetry, Silver amalgam film electrode.

Introduction

The intensive use of herbicides and other classes of chemicals products in agricultural practices has resulted in serious impacts on the environment, causing an increase in the level of herbicide residues in natural water, soil, river sediments, and foodstuffs [1, 2]. Among the herbicides frequently used, flumetralin (N-(2-chloro-6-fluorobenzyl)-N-ethyl-α,α,α-trifluoro-2,6-dinitro-p-toluidine, Fig. 1) is a selective herbicide applied toward systemic sucker control in plants therefore decreasing the need for manual removal and increasing plant's yield and quality.
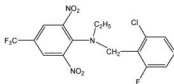

Fig. 1. Chemical structure of flumetralin.

Literature survey showed that only chromatographic methods have been developed for FLM determination so far [3-11]. Electroanalytical methods are simple, economical, rapid and sensitive enough to reach required low limits of detection for trace analysis of various inorganic and organic compounds. Among the electroanalytical techniques, voltammetry coupled with pulse waveform, e.g., square wave voltammetry (SWV) is considered as a highly sensitive technique with very low detection profiles attributed to zero background current. In our research, SWV was coupled with a variant of silver amalgam film electrode,

capable of repetitive and reproducible renewing of the electrode surface. Construction of the Hg(Ag)FE, its features and the principles of its operation were described in detail formerly [12-14]. The use of silver amalgamate enables the electrode to work for a few months in a stable manner [15]. The feature of preserving the properties of the mercury electrode with consuming a very small amount of mercury (about 1 μL on 1000 measurement cycles) is the main advantage of above mentioned electrode. This work is aimed at developing a simple and sensitive electroanalytical method for the flumetralin determination and its application in analysis of water samples.

Experimental

Apparatus

All voltammetric experiments were performed with MultiAutolab Potentiostat (EcoChemie, Netherlands) through electrochemical software NOVA 1.10.3. A three-electrode cell was employed incorporating Hg(Ag)FE electrode (AGH University, Cracow), Ag/AgCl (3.0 M KCl) reference electrode and platinum wire counter electrode. Amalgam electrode surface was mechanically refreshed before each measurement. Refreshing procedure is thoroughly discussed in literature [14]. Moreover, conditioning potential -0.9 V was applied to electrode for 6 s before recording each measurement. Stirring of the solutions was achieved with a Teflon-coated magnetic stirrer operated by M164 stand (mtm-anko). Measurements of pH were made using a pH-meter (Elmetron, Poland) with a combined glass electrode. All experiments were performed at room temperature 20 ± 2 °C.

Solutions

All reagents were of analytical grade and demineralized double distilled water was used in all experiments. Flumetralin was purchased from Sigma Aldrich (St. Louis, MO) and used for preparing 25 mL of a 1.00×10^{-3} mol L^{-1} stock standard solution by dissolving 10.54 mg of FLM in ethanol. Working solutions of lower concentrations were freshly prepared by the appropriate dilution of the stock standard solution. Britton–Robinson (BR) buffer solutions of different pH values were prepared by the addition of sodium hydroxide solution to a phosphoric, boric and acetic acid mixture. The final pH was checked using a pH-meter.

Voltammetric procedure

Supporting electrolyte consisting of nine milliliters of 0.04 M BR buffer solution (pH 9.5) and 1 mL of 1 mM CTAB containing a specific amount of standard solution of FLM was added to an electrochemical cell. Oxygen dissolved in solutions was removed by passing pure argon. Electrochemical measurements of FLM ware carried out by SWSV and recorded in the potential range from -0.2 to -1.0 V. The SWV parameters were as follows: frequency 50 Hz, step potential 5 mV, amplitude 40 mV, accumulation potential -0.2 V and accumulation time 60 s.

Results and Discussion

Influence of pH and parameters of SWSV

The square wave stripping voltammograms of flumetralin showed two well-defined cathodic signal, one at E = -0.5 V and second around E = -0.4 V (Fig. 2A). For analytical purposes and construction of calibration curve, signal with more negative potential was chosen.
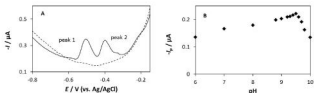
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Fig. 2. SW voltammograms for $5 \cdot 10^{-6}$ mol L^{-1} FLM solution in Britton-Robinson buffer (pH 9.5), frequency 50 Hz, step potential 5 mV, amplitude 40 mV (**A**). Dependence of flumetralin peak 1 current intensity on pH (**B**).

The electrochemical behavior of FLM was investigated over the pH range from 2.0 to 10.0 in 0.04 M BR buffer solution (Fig. 2B). In solutions with pH lower than 6.0, FLM signals were not observed. The relationship between the peak current and pH was investigated. As can be seen the peak current in pH 9.5 is at maximum. Therefore, this value was chosen as the optimum pH and used in all the subsequent experiments. The peak potentials shifted to the negative values with increasing pH. The negative shift in cathodic peak potential with pH can be described by the following equations for peak 1 and 2: $E_1 = 0.0479 - 0.0595$pH, $r = 0.9931$ and $E_2 = 0.1698 - 0.0611$pH, $r = 0.9952$, respectively. The slopes of the drawn regressions are close to the theoretical value of 59.0 mV pH^{-1}.

The optimization of SWSV parameters for determination of flumetralin was also carried out. The results show significant influence of square wave voltammetric parameters on the FLM reduction signals. The current response of FLM increased linearly with amplitude up to 40 mV, above this value nonlinear growth of the signal (plateau) was observed. SW frequency (*f*) was changed in the range from 8 to 251 Hz. In this range, linear dependence between *f* and peak current was observed. Frequency values higher than 50 Hz caused significant signal deterioration. The peak shape and current response for FLM was also greatly affected by varying step potential values, taking into account the signal shape for analytical purposes, step potential equal to 5 mV was chosen for further studies. Next, stripping parameters (accumulation time and potential) were optimized. The highest signals were obtained with accumulation potential -0.2 V and accumulation time of 60 s. Thus, for determination of FLM the optimal values of SWSV parameters were found to be: frequency 50 Hz, amplitude 40 mV, step potential 5 mV, accumulation potential -0.2 V, and accumulation time 60 s.

Calibration curve

The relationship between the cathodic peak current and FLM concentration was examined over the range $5 \cdot 10^{-9}$ mol L^{-1} - $1 \cdot 10^{-7}$ mol L^{-1} in 0.04 M BR buffer solution (pH 9.5). The linear relationship between i_{pa} and c_{FLM} is expressed with regression equation i_{pa} [µA] = 11.83c_{FLM} [mol L^{-1}] + $4 \cdot 10^{-9}$ ($r - 0.9976$). Calculated LOD and LOQ were found to be $6.43 \cdot 10^{-10}$ and $2.15 \cdot 10^{-9}$ mol L^{-1}, respectively.

Tap water analysis

Tap water was spiked with concentration of $3 \cdot 10^{-8}$ mol L^{-1}. Standard addition method was used to determine FLM in spiked tap water. Six replicate experiments were performed. Exemplary voltammogram obtained during determination is shown in Fig. 3. Analysis results are summarized in the Table I.
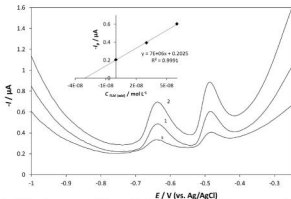
Fig. 3. SWS voltammograms of flumetralin determination in spiked tap water sample using the standard addition method (s – sample; 1, 2 – standard additions). Experimental conditions are the same as in Fig. 2 and deposition potential and time -0.2 V and 60 s, respectively. Inset: Curve for evaluation of standard additions.

Table I.
Results of flumetralin determinations in spiked water samples.

Series	c [mol·L^{-1}]	Error	Recovery [%]
1	3.04×10^{-8}	0.014	101.5
2	3.01×10^{-8}	0.004	100.5
3	2.98×10^{-8}	0.004	99.61
4	3.09×10^{-8}	0.030	103.1
5	3.00×10^{-8}	0.000	100.0
6	3.16×10^{-8}	0.053	105.4
$C \pm SD(k,\alpha)$ [mol·L^{-1}]	$3.05 \times 10^{-8} \pm 6.69 \times 10^{-10}$	CV [%]	Average recovery [%]
		2.2	101.7

Conclusion

The above results clearly demonstrate the potential utility of the Hg(Ag)FE electrode for square wave stripping voltammetric determination of flumetralin. Additionally, the proposed procedure is fast, of high precision and accuracy and can be employed for quantification of FLM in water samples, where the results showed no influence of the matrices on the current response. All the results obtained using the optimized experimental and voltammetric parameters confirmed the practicality and viability of the proposed procedure, providing an important tool for quantification of FLM in water samples. The use of SWSV is faster and more sensitive than other conventional techniques.

Acknowledgements

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