CHRONOPOTENTIOMETRIC DETERMINATION OF METAMITRON: COMPARING CLASSICAL AND BOX-BEHNKEN OPTIMIZATION APPROACHES

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Abstract
This paper describes an optimization procedure for determination of the herbicide metamitron by chronopotentiometry. Two different working electrodes were use in the experiments: glassy carbon and thin film mercury electrode. The analytical signal of metamitron was the result of irreversible reduction on the working electrodes in Britton-Robinson buffer as the supporting electrolyte, and one reduction peak was obtained on both working electrodes. Operating conditions, involving several chemical and instrumental parameters such as: pH of Britton-Robinson buffer, initial potential and reduction current were optimized by the classical method, where one parameter is changing while others are constant, and by using Box-Behnken experimental design. In both optimization procedures, the maximum height of the metamitron analytical signal was requested. Obtained results from this study revealed that there were no differences between the two optimization methods.

Introduction
Metamitron (IUPAC: 4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one, MTM) is a selective triazinone herbicide that is often used nowadays in agriculture for weed control in a variety of crops [1]. Like other pesticides, it can be toxic for humans, especially for aquatic organisms [2]. After application, the herbicide is predominantly absorbed by the roots, and also by leaves, and it acts as an inhibitor of photosystem II by induction chlorotic and necrotic symptoms in leaves [1, 3]. Depending on the environmental conditions: temperature, moisture, soil type, and application dose observed half-life for MTM in soil in the literature ranges from 6 to 90 days [3, 4]. High solubility in water (1.7 g/dm^3) and weak sorption of MTM in soils with low organic matter content indicates the possibility of leaching and pollution of ground water sources [1, 5-7]. Hence, this herbicide was frequently detected in surface in ground water in concentrations up to 1.5 μg/dm^3 [8-10].
Several methods have been reported in the literature for the determination of MTM such as chromatography [3, 8, 10-13] and spectroscopy [14]. These methods have proven to be sensitive and reliable, but also limited in the portability of sophisticated instrumentation, resulting in high cost and long detection time [15]. Nowadays, the use of electroanalytical procedures can be a suitable alternative, offering easy instrumental manipulation, low operating costs and accurate results with short analysis time. Square wave voltammetry [16, 17] and differential pulse voltammetry [18, 19] are the most frequently applied electroanalytical procedures for MTM determination.
The optimization procedure in most cases is carried out by monitoring the influence of one factor, while others are kept at constant level, in thus so called classical way. The major disadvantages of this kind optimization technique are increased number of experiments, and consumption of chemicals [20]. Also, this optimization technique does not consider the interactive effects among the studied parameters, which can lead to incorrect results. In past decade, response surface methodology with Box-Behnken experimental design has been

frequently applied in the optimization of analytical methods [21-23]. In this paper, glassy carbon electrode (GCE) and thin film mercury electrode (TFME) are used for chronopotentiometric determination of MTM. Results of two different optimization protocols using traditional and response surface methodology with Box-Behnken design are compared.

Experimental

All electrochemical measurements were carried out in a three-electrode system with M1 analyser for potentiometric and chronopotentiometric measurements constructed by our laboratory. GCE was used as the working electrode, or as an inert support for TFME. The auxiliary electrode was a platinum wire (φ = 0.7 mm, l = 7 mm), and the reference was an Ag/AgCl (3.5 mol/dm^3 KCl) electrode. The GCE surface was polished with alumina slurry Al_2O_3 (0.5 μm) and sonicated in mixture of ethanol and doubly distilled water for 10 min. TFME was prepared ex situ from the 0.02 mol/dm^3 HCl solution containing 0.15 g/dm^3 of Hg^{2+} ions at the potential of -0.4 V for 240 s, with stirring the solution.

Electrodes were immersed into the 20 dm^3 of the supporting electrolyte, and the solution was purged with a nitrogen stream for 5 min before recording chronopotentiograms. Then, MTM standard solution was added to the supporting electrolyte and nitrogen stream was passed through the solution for additional 30 s. Afterwards, chronopotentiograms with the appropriate MTM reduction time were recorded.

MTM stock solution (0.01 mol/dm^3) was prepared by dissolving of solid chemical (Dr Ehrenstorfer, Augsburg, Germany) in the HPLC grade acetonitrile (Kemika, Zagreb, Croatia). Working solution (0.04 mol/dm^3) was prepared by appropriate dilution of the stock solution in doubly distilled water. Britton-Robinson (BR) buffers in the pH range from 2 to 12 are prepared by adding equal molls (0.04 mol) of boric, phosphoric and acetic acid. Sodium hydroxide (0.2 mol/dm^3) was employed to adjust pH value of the buffer. All other reagents were of analytical grade.

Results and discussion

Classical optimization methodology

The effect of pH on the reduction time was investigated in BR buffer by applying pH values from 2 to 12, while the concentration of MTM was in the range from 2 mg/dm^3 to 10 mg/dm^3. Using the GCE as the working electrode, the best sensitivity was obtained from pH 2 to 4, with a significant decrease of reduction time from 2.15 s to 1.59 s (Table 1). In BR pH 5 only concentrations of herbicide higher than 2 mg/dm^3 could be detected, therefore this value of pH is not included in further experiments. When MTM was investigated using TFME as a working electrode, the analytical signal is obtained in the range of pH of BR buffer from 2 to 10, while the best defined signals and highest sensitivity are accomplished in pH range from 5 to 9 (Table 1). As optimal pH values of BR buffer selected are those where the highest signal is obtained with best reproducibility and sensitivity. For GCE pH 2 was accepted as optimal, while for TFME pH 7 was proved as optimal.

The effect of initial potential on the MTM analytical signal using GCE was examined in the BR buffer pH 2 containing 10 mg/dm^3 MTM, in the potential range from 0.01 V to -0.63 V. Change of initial potential from 0.01 V to -0.45 V did not significantly affect the height of the analytical signal, while at the initial potential of -0.63 V the analytical signal significantly decreased. As optimal value of the initial potential -0.31 V was accepted. Using TFME as a working electrode the influence of initial potential on the MTM analytical signal was investigated in BR pH 7 containing 10 mg/dm^3 MTM in the potential range from 0 V to -0.51 V. In the investigated potential range MTM reduction time decreased from 0.95 s to 0.75 s, and the worst reproducibility is obtained at the value of -0.14 V. The highest and the most

reproductive analytical signal of MTM was obtained at the value of initial potential of 0 V (τ_{red} = 0.95 s, RSD = 1.49%, Figure 1), and this value is accepted in all further experiments.

Table 1. The effect of pH of BR buffer on the MTM analytical signal, on GCE and TFME, concentration of MTM 10 mg/dm^3

Working electrode	pH of BR buffer	Reduction time ± 2 SD (s)[a]
GCE	2	2.15 ± 0.02
	3	1.75 ± 0.03
	4	1.59 ± 0.02
TFME	5	0.61 ± 0.02
	6	0.65 ± 0.04
	7	1.16 ± 0.03
	8	1.13 ± 0.03
	9	1.02 ± 0.03

[a] n =3.

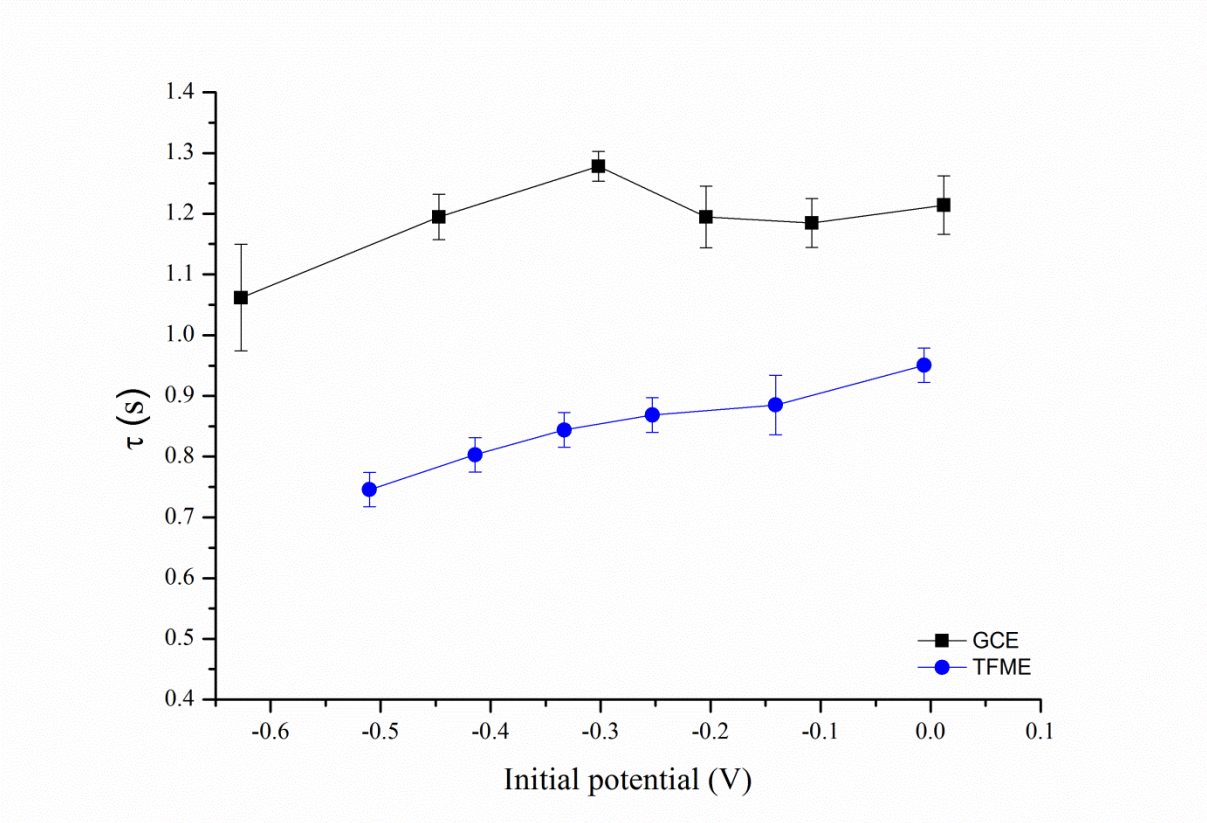

Figure 1. The effect of initial potential on the MTM analytical signal on GCE and TFME, concentration of MTM 10 mg/dm^3, mean ± 2SD, n = 3

In chronopotentiometry the reduction current represents the most important parameter of the analysis, as it heavily influences on the height and sharpness of the analytical signal. Studied ranges of reduction current for solutions containing 10 mg/dm^3 MTM on GCE and TFME were from -1.9 µA to -7.9 µA, and from -3.5 µA to -16 µA, respectively. The MTM reduction time decreased exponentially with more negative values of reduction current for both working electrodes used in experiments. Obtained exponential functions for GCE and TFME were $\tau = 2.2576\ e^{0.1182\ i}$ r = 0.9973, and $\tau = 4.2113\ e^{0.2597\ i}$ r = 0.9974, respectively. Using the criterion of rectilinear sequence of dependence I $\tau_{red}^{1/2}$ = f (I), the appropriate intervals of reduction current that should be applied for MTM determination were from -1.9 to -7.9 µA for GCE, and from -3.5 to -14.3 µA for TFME.

Box-Behnken optimization method

Using the preliminary results of the classical optimization methodology, where a measurable signal of the analyte is obtained, a three-level three-factor Box-Behnken experimental design was used for optimization procedure. Chronopotentiometric experiments were performed in Britton-Robinson buffer using the reduction time of 10 mg/dm^3 of MTM as the response of the system. The statistical analysis involves the significance of the parameters, and their interactions on the analytical signal has been described in detail elsewhere [24]. Based on the obtained results, the maximum analytical signals are obtained by the following combination of parameters: pH of BR buffer 2, initial potential -0.31 V, reduction current -2.3 μA for GCE, and pH of BR buffer 7, initial potential 0 V, reduction current -3.5 μA for TFME. By comparing the results of the classical optimization procedure with the results obtained using the experimental design, no differences in the optimal parameters of the analysis were observed.

Conclusion

This paper describes optimization procedures for chronopotentiometric determination of the herbicide MTM using GCE and TFME as working electrodes. In the first step, the optimization was performed in the classical way by changing one factor, while the others are maintained at a constant level. The results obtained using the classic optimization methodology, are compared with the results obtained on the basis of the Box-Behnken experimental design and the statistical analysis. In the light of findings from both optimization procedures, it can be concluded that they presenting similar results. The developed method could be applied for determination of the MTM content in real samples.

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