

Research Article

First Electrochemical Method of Nitrothal-Isopropyl Determination in Water Samples

Dariusz Guziejewski,¹ Agnieszka Nosal-Wiercińska,²
Sławomira Skrzypek,¹ Witold Ciesielski,¹ and Sylwia Smarzewska¹

¹Department of Inorganic and Analytical Chemistry, University of Lodz, Lodz, Poland

²Department of Analytical Chemistry and Instrumental Analysis, Maria Curie-Skłodowska University, Lublin, Poland

Correspondence should be addressed to Dariusz Guziejewski; dguziejewski@uni.lodz.pl

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The aim of the research was the use of square wave adsorptive stripping voltammetry (SWAdSV) in conjunction with a hanging mercury drop electrode (HMDE) for the determination of nitrothal-isopropyl. It was found that optimal SW technique parameters were frequency, 200 Hz; amplitude, 50 mV; and step potential, 5 mV. Accumulation time and potential were studied to select the optimal conditions in adsorptive stripping voltammetry: 45 s at 0.0 V, respectively. The calibration curve (SWSV) was linear in the nitrothal-isopropyl concentration range from 2.0×10^{-7} to 2.0×10^{-6} mol L⁻¹ with detection limit of 3.46×10^{-8} mol L⁻¹. The repeatability of the method was determined at a nitrothal-isopropyl concentration level equal to 6.0×10^{-7} mol L⁻¹ and expressed as RSD = 5.5% ($n = 6$). The proposed method was successfully validated by studying the recovery of nitrothal-isopropyl in spiked environmental samples.

1. Introduction

The agricultural practices intensively use pesticides, herbicides, fungicides, and other classes of chemical products to achieve maximal productivity. This has resulted in serious impacts on the natural environment, causing an increased level of pollutant residues in water, soil, river sediments, and foodstuffs [1, 2]. The elaboration of modern, easy-to-operate, rapid, sensitive, and inexpensive methods for the detection of hazard residues in the environment is a main task in analytical chemistry nowadays. Many published articles report the pollutants determination in natural samples, mainly using separation and spectrometric methods [3].

Fungicides are biocides that are usually applied to protect fruits and vegetables against fungi. The increased risk of fungicide residues accumulation can cause serious health problems also through human exposure to their remnants present in the food. Among the fungicides used, nitrothal-isopropyl (diisopropyl 5-nitroisophthalate, NT, Figure 1) is a selective fungicide applied towards control of the development of many side effects of diseases caused by

microorganisms in plant breeding of agricultural crops. It has been applied for the control of *Podosphaera leucotricha* in apple trees, *Phytophthora infestans* in tomato and potato, and *Septoria apii* in celery as well as *Bremia lactucae* in lettuce cultivation. Nitrothal-isopropyl is also applied as a seed treatment, in order to combat diseases of vegetable and ornamental plants. It is used in forestry for diseases causing needles drooping as well. In humans NT can cause eyes, skin, and respiration system irritation. Nitrothal-isopropyl is classified as a third-class toxicity pesticide for mammals.

The most common methods of NT determination employ gas, liquid or thin-layer chromatography and selective detector [4–8]. Voltammetric techniques are described with several advantages like wide linear concentration range, good sensitivity, low apparatus cost, capability of miniaturization, capability for on-site detection, relatively short time of analysis, and insensitivity to matrix effects [9, 10]. Hanging mercury drop electrode commonly used for characterization of electrode processes and analytical purposes can be characterized with wide range of potential in a negative region, easily renewable and smooth surface, capability

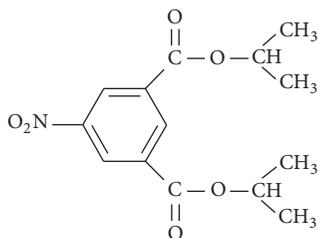


FIGURE 1: Chemical structure of nitrothal-isopropyl.

for preconcentration of analytes, and so forth. Moreover square wave voltammetry (SWV) is recognized as the most frequently used voltammetric technique for electroanalysis [11]. Pulsed voltammetric techniques are acknowledged with relatively low detection profiles ascribed to low background current. The electroanalytical techniques have long history in applications towards analysis of biocides in different environmental matrices [12–15]. Electroanalytical techniques are also advantageous due to characterization possibilities in kinetic and equilibrium studies [16–19]. Investigation of nitro-group containing compounds using voltammetric methods has been utilized since the very beginning of polarography [20] and voltammetry [21]. Despite the increased fears of liquid mercury toxicity in the past years, a stable attention is given to the development of electroanalytical methods that utilize hanging mercury drop [22] or amalgam electrodes [23–25]. The most common electrode reaction involves two-step mechanism corresponding initially to a four-electron reduction of the NO_2 group and the second signal with the reduction of the previously formed hydroxylamine group to the NH_2 group involving two electrons [26]. There are also possible other reaction mechanisms depending on the type of electrode material, supporting electrolyte pH, and so forth. Due to high hydrogen overpotential mercury-based working electrodes were found suitable for voltammetric determination of nitroaromatic molecules.

Up to date there was no voltammetric work dealing with elaboration of electroanalytical method of nitrothal-isopropyl determination. Thus the goal of this work was aimed at the development of a simple and sensitive method for the aforementioned fungicide determination.

2. Experimental

2.1. Apparatus. All electrochemical measurements were performed with microAutolab potentiostat (EcoChemie, Netherlands) through electrochemical software version GPES 4.9. A three-electrode cell was employed incorporating a hanging mercury drop electrode (AGH University, Cracow), an Ag/AgCl (3.0 M KCl) reference electrode, and a Pt wire as a counter electrode. No special pretreatment of electrochemical station was needed prior to the measurements except degassing the working solution in the voltammetric cell with pure argon (5 N). Mass transport 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 $20 \pm 1^\circ\text{C}$.

2.2. Solutions. All chemicals used were of analytical grade. Double distilled demineralized water was exploited throughout experiments. Nitrothal-isopropyl was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and used as received. 25 mL of a 1.00 mmol L^{-1} stock standard solution was prepared by dissolving 7.41 mg of NT in a mixture of ethanol and water (1:1, v:v). Solutions with higher dilution were freshly prepared before measurements from 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 while citrate buffers were composed of sodium citrate in combination with required amount of hydrochloric acid. The final pH was controlled and adjusted using a pH-meter.

2.3. Voltammetric Procedure. 10 mL of buffer solution was placed in an electrochemical cell containing a specific amount of analyzed NT standard solution. In order to remove dissolved oxygen degassing was performed before each measurement by passing through an argon stream. Electrochemical measurements of nitrothal-isopropyl were carried out with SWSV and recorded in the potential range from 0.0 to 2.0 V. The SW voltammetric parameters were as follows: frequency 200 Hz, step potential 5 mV, and amplitude 50 mV with accumulation at 0.0 V for 45 s.

3. Results and Discussion

3.1. Electrochemical Behavior. Nitrothal-isopropyl is an electroactive compound and square wave adsorptive stripping voltammograms recorded in its presence show two well-defined reduction signals, first close to -0.1 and second approximately at -0.6 V (Figure 2). For analytical purposes signal at less negative potential value was chosen due to increased sensitivity caused by higher response.

The influence of the supporting electrolyte pH on the electrochemical behavior of nitrothal-isopropyl was evaluated with the peak potential and current analysis. The electrochemical reduction of NT was investigated in the pH range 2.0–12.0 in 0.04 M BR buffer solution (inset in Figure 2). NT signals were observed in the whole studied pH range. The observed analytical peak current was highly dependent on the supporting electrolyte pH. The maximum peak current was observed at pH 2.5. The peak potentials shifted significantly towards more negative values with pH increment. The cathodic peak potential relocation can be specified with the following equation: $E_p \text{ (V)} = 0.017 \text{ (V)} - 0.046 \cdot \text{pH}$; $r = 0.998$. The slope of those dependencies is close to the theoretical value of 59.0 mV pH^{-1} and suggests protons involvement in the electroreduction of nitrothal-isopropyl most probably with equal number as electrons. The same analysis was performed in citrate buffer in the pH range 1.5–3.5 where the highest signal was again observed at pH 2.5. As can be seen (Figure 2(b)) observed peak current is much

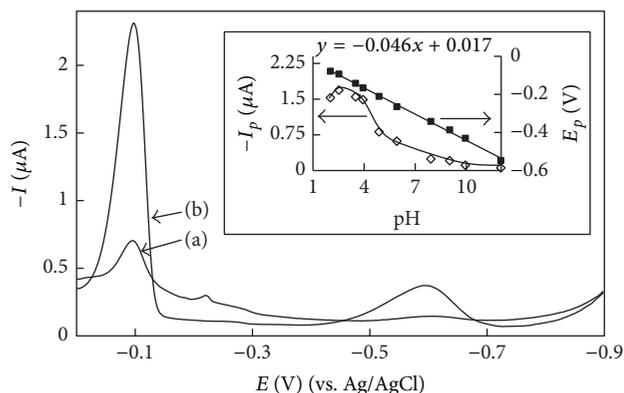


FIGURE 2: SW voltammograms for 2×10^{-6} mol L $^{-1}$ NT solution in citrate (a) and Britton-Robinson (b) buffer (pH = 2.5), frequency 50 Hz, step potential 5 mV, and amplitude 50 mV. Inset presents pH dependence of nitrothal-isopropyl analytical peak current intensity and position in BR buffer.

higher in BR buffer and therefore this supporting electrolyte with pH 2.5 was selected and applied in further experiments.

The optimization of square wave adsorptive stripping voltammetric parameters for nitrothal-isopropyl determination was a crucial step in preparation of electroanalytical method. The results show significant influence of square wave voltammetric parameters on the NT reduction signals (data not shown). The step potential (ΔE_s), the amplitude (ΔE), and the frequency (f) were studied within the variable ranges of 1–7 mV, 10–140 mV, and 8–500 Hz, respectively. The peak shape and current response for NT were greatly affected by varying step potential values. Taking into account signal shape for analytical purposes, step potential equal to 5 mV was chosen for further studies. The current response of NT increased linearly with amplitude up to 40 mV; above this value minor regression of the signal was noticed. Also ratio between peak current and half peak width suggests this value as optimal amplitude. In the range of studied square wave frequencies a nonlinear dependence between f and peak current was observed. Significant signal shape deterioration was caused when frequency values higher than 250 Hz were applied. Keeping also in mind that the background current increases at higher frequencies an optimal value of 200 Hz was selected. Thus, for determination of NT the optimal values of square wave voltammetric parameters were found to be frequency 200 Hz; amplitude 40 mV; and step potential 5 mV. Next, stripping parameters were optimized in the range 0–180 s and 0.25––0.05 V for accumulation time (t_{acc}) and potential (E_{acc}), respectively. E_{acc} of 0.0 V was found to be suitable since the peak current was gradually increasing with accumulation potential shift towards less positive value and a significant drop of the signal at $E_{acc} = -0.05$ V was observed. The dependence of peak current on accumulation time shows constant increments in the peak current up to 45 s and further continuous decline. In both cases the peak position shifted slightly towards more negative potentials when increasing analyzed parameter. As the most optimal accumulation potential 0.0 V and time 45 s were selected.

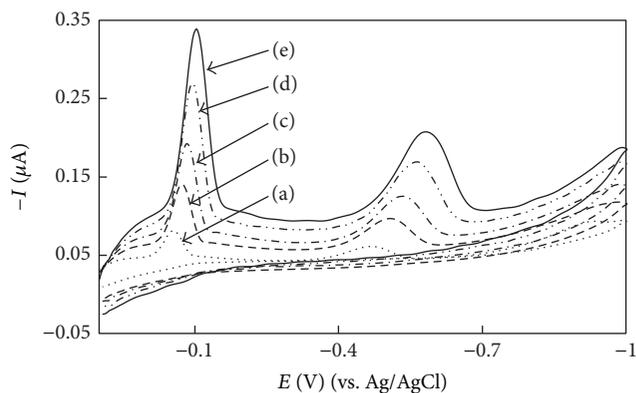


FIGURE 3: Cyclic voltammograms for 5.0×10^{-6} mol L $^{-1}$ NT solution in Britton-Robinson buffer (pH = 2.5) at the scan rates (a) 20, (b) 75, (c) 150, (d) 300, and (e) 500 mV s $^{-1}$.

Cyclic voltammetry was used to study the NT electrochemical behavior. The potential scan was started at pH 2.5 from 0.0 V to the negative direction and reversed at -2.0 V back to the starting potential. As can be seen in Figure 3 NT manifests two separated reduction peaks, related to irreversible two-step process as there is no evidence of corresponding oxidation signal. The influence of scan rate on NT peak current was investigated from 20 to 500 mV s $^{-1}$ as well. When the scan rate increased, cathodic peaks shifted in more negative direction as expected from an irreversible reaction. Linear dependence between peak current and square root of scan rate was observed ($I_p = -3.74 \times 10^{-7} v^{1/2} - 1.8 \times 10^{-8}$, $r = 0.999$) indicating diffusional nature of electrode processes. It was confirmed by constructing the plot of logarithm of peak intensity (μA) versus the logarithm of scan rate (V/s). The equation was $\log I_p (\mu A) = 0.58 \log v (V s^{-1}) - 6.43$ ($r = 0.989$). Calculated slope for this dependence was close to 0.5 which is attributed to processes controlled by diffusion [27, 28].

The above-described cyclic voltammograms, pH effect, and literature survey on the reduction of aromatic nitro compounds [22, 25, 29, 30] suggest the following electrode reaction mechanism. The reduction peak appearing at less negative potential could be attributed to the reduction of the $-NO_2$ group through a single four-electron four-proton irreversible step into NHOH group. Furthermore, the next peak corresponds to further reduction of hydroxylamine group to an appropriate amino group with involvement of both two protons and two electrons.

3.2. Electroanalytical Application. The dependence between the cathodic peak current and NT concentration was examined using SWAdSV (Figure 4). A linear relationship was observed over the range from 2×10^{-7} to 2×10^{-6} mol L $^{-1}$ in 0.04 M BR buffer solution (pH 2.5) under the optimum conditions. The calibration curve was calculated using least square equation. Table 1 provides the characteristic of the calibration plot.

The LOD and LOQ values of the method were obtained based on kSD/b ($k = 3$ for LOD, $k = 10$ for LOQ, resp.,

TABLE 1: Quantitative determination of nitrothal-isopropyl in BR buffer; pH = 2.5 with SWSV. Basic statistic data of the regression line.

Linear concentration range (mol L^{-1})	2.00×10^{-7} – 2.00×10^{-6}
Slope of calibration graph (A L mol^{-1})	4.28 ± 0.08
Intercept (μA)	0.11 ± 0.01
Correlation coefficient	0.999
Number of measurements	6
LOD (mol L^{-1})	3.46×10^{-8}
LOQ (mol L^{-1})	1.15×10^{-7}

TABLE 2: Recovery and precision of the NT peak currents at various nitrothal-isopropyl concentrations.

Concentration		Precision CV [%]	Recovery [%]
Given [$\mu\text{mol L}^{-1}$]	Found		
0.200	0.202	1.4	101
0.400	0.389	3.7	97.3
0.600	0.577	5.5	96.3
0.800	0.816	3.7	102
1.00	1.02	3.4	103
2.00	1.99	1.8	99.5

where SD = standard deviation of the intercept, b = slope of the calibration curve) [31]. The LOD value was well enough below the lethal dose for most of living organisms (e.g., $\text{LC}_{50} = 0.33 \text{ mg L}^{-1}$ in the case of trout) in natural water [32] and reflects the sufficient sensitivity of the method. The precision and recovery of the method were measured from six repeated measurements of the NT electrochemical signal at different concentrations (Table 2).

3.3. Interferences. The proposed method selectivity was investigated and evaluated with the addition of heavy metal ions, pesticides, or fungicides. The concentration of each possible interferent was increased from 1.0×10^{-8} through 5.0×10^{-8} , 1.0×10^{-7} , 5.0×10^{-7} , and 1.0×10^{-6} up to $5.0 \times 10^{-6} \text{ mol L}^{-1}$. The recorded voltammograms were compared with the result obtained only in the presence of NT solution at a concentration of $5.0 \times 10^{-7} \text{ mol L}^{-1}$. The presence of cadmium, lead, and cobalt ions did not interfere with NT voltammetric response at any of the investigated concentrations. Dodine, dinotefuran, and cyromazine also had no interference action in the studied concentration range despite presence of their signals at about -1.1 V . Clothianidin precluded nitrothal-isopropyl proper determination only at the highest investigated concentration although its signals were observed from the beginning at -0.6 , -0.85 , and -1.1 V . Strong adsorption of acibenzolar-S-methyl and metam sodium at the concentration $5.0 \times 10^{-7} \text{ mol L}^{-1}$ and higher at the electrode surface caused severe drop of recorded NT voltammetric signal, although their signals present at -0.5 , -1.0 , and -0.3 , -0.5 V , respectively did not interfere with nitrothal-isopropyl voltammetric signal. These results suggest that in most cases

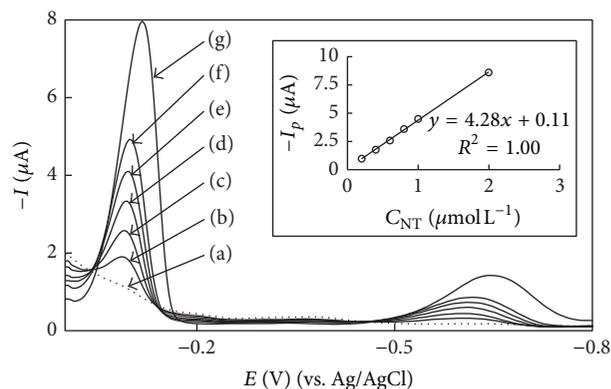


FIGURE 4: SWAdS voltammograms recorded in BR buffer pH 2.5 with increasing nitrothal-isopropyl concentration $C_{\text{NT}} = 0$ (a), 2.0×10^{-7} (b), 4.0×10^{-7} (c), 6.0×10^{-7} (d), 8.0×10^{-7} (e), 1.0×10^{-6} (f), and $2.0 \times 10^{-6} \text{ mol L}^{-1}$ (g). The other experimental conditions were SW amplitude 50 mV, step potential 5 mV, frequency 200 Hz, accumulation time 45 s, and accumulation potential 0 V. Inset: corresponding calibration line.

the method is selective and can be used in cases of simple environmental samples without significant deterioration.

3.4. Analysis in Spiked Water Samples. Water samples were spiked with nitrothal-isopropyl at the $4.0 \times 10^{-7} \text{ mol L}^{-1}$ concentration. Six replicate experiments were performed along with standard addition method to determine NT in spiked environmental samples. Exemplary voltammograms obtained during studies are presented in Figure 5. The consecutive standard additions of nitrothal-isopropyl have caused respective increments on the related peak at -100 mV (Figure 5). No matrix effects nor signal shifting/deteriorations were visualized. The reliability of the proposed square wave voltammetric method was investigated by assaying nitrothal-isopropyl in water samples. A series of water samples were used to further investigate the accuracy of the proposed method. Analysis results are summarized in Table 3. The received results imply that the evaluated method is accurate, selective, and precise sufficiently enough to be introduced in routine analysis.

4. Conclusion

The above-described data clearly demonstrate the possible use of the hanging mercury drop electrode for square wave adsorptive stripping voltammetric determination of nitrothal-isopropyl. Since the proposed methodology is fast and of high precision and accuracy therefore it can be used for NT quantification in water samples with no matrix effects on the measurable response. All the data received using the optimized experimental conditions and voltammetric parameters acknowledged the practical application and viability of the proposed methodology, ensuring a new instrument for quantification of NT in water samples. The use of SWAdSV is usually more efficient than other conventional techniques. The newly developed procedure allows accurate detection of nitrothal-isopropyl and introduces a simple, fast, selective,

TABLE 3: Results of NT determination in spiked samples with SWAdSV.

Sample	Concentration given [mol L ⁻¹]	Concentration found [mol L ⁻¹]	CV [%]	Recovery [%]
Tap water	4.0 × 10 ⁻⁷	(4.1 ± 0.5) × 10 ⁻⁷	4.8	102
River water (Jasień)		(4.2 ± 0.1) × 10 ⁻⁷	2.2	104

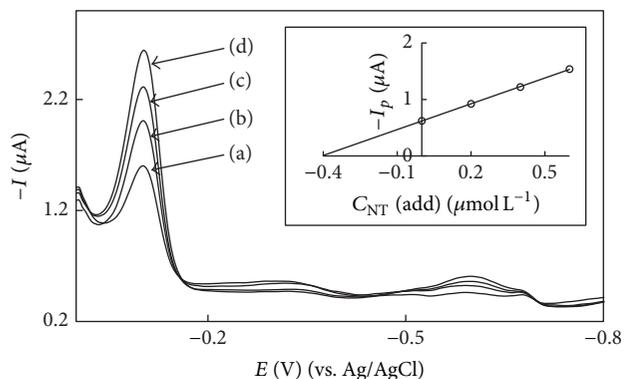


FIGURE 5: SWAdS voltammograms of nitrothal-isopropyl determination in spiked tap water samples using the standard addition method ((a) sample; (b), (c), and (d) standard additions). Experimental conditions are the same as in Figure 4. Inset: corresponding calibration curve.

and highly sensitive methodology. The capability to determine the fungicide content directly from the matrix medium or natural samples without any laborious pretreatment which are usually time-consuming and environmentally unfriendly is one of the main advantages of the method.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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