

Hülya Mercan<sup>1</sup>  
Recai İnam<sup>2</sup>

<sup>1</sup>Faculty of Art and Science,  
Department of Chemistry, Ahi Evran  
University, Kırşehir, Turkey

<sup>2</sup>Faculty of Art and Science,  
Department of Chemistry, Gazi  
University, Ankara, Turkey

## Research Article

# Determination of Cymoxanil Fungicide in Commercial Formulation and Natural Water by Square-wave Stripping Voltammetry

Voltammetric behavior of cymoxanil fungicide dissolved in water–acetonitrile (1:1) solution was investigated by square-wave stripping voltammetry (SWSV) and cyclic voltammetry (CV). The cymoxanil was accumulated at  $-400$  mV on a hanging mercury drop electrode (HMDE) and a well-defined cathodic peak obtained at  $-680$  mV (pH 7.0). The optimal experimental parameters for the cymoxanil assay were an accumulation potential of  $-400$  mV (vs. Ag/AgCl/KCl), accumulation time 10 s, frequency 350 Hz, and pulse amplitude 75 mV. The cyclic voltammetric measurements showed an irreversible nature of the reduction wave at HMDE in the range of scan rates comprised between 5 and 4000 mV/s. The calibration curve obtained from SWSV was linear in the range 23.6–1950  $\mu\text{g/L}$  with a detection limit of 7.1  $\mu\text{g/L}$ . The method was applied to the direct determination of fungicide in water samples. Recoveries calculated for river and tap water samples spiked with 40  $\mu\text{g/L}$  level were  $40.2 \pm 0.8$  and  $39.8 \pm 0.9$   $\mu\text{g/L}$  at 95% confidence level, respectively. The method was extended to determination of cymoxanil in agrochemical formulation Tri-Miltox Max<sup>®</sup> with recovery of 102.5%. The sufficiently good recoveries and low relative standard deviations reflect the high accuracy and precision of the proposed square-wave voltammetric method. Influences of some interfering species were also investigated.

**Keywords:** Cymoxanil; Determination; Fungicide; Pesticide; Square-wave stripping voltammetry

*Received:* January 27, 2010; *revised:* March 5, 2010; *accepted:* April 10, 2010

**DOI:** 10.1002/clen.201000038

## 1 Introduction

Cymoxanil (2-cyano-N-[(ethylamino) carbonyl]-2-(methoxyimino)acetamide) is a aliphatic nitrogen fungicides. It is applied as a seed treatment to cut potato seed pieces or as a foliar application to the plants to control late blight (*Phytophthora infestans*) [1]. On a worldwide basis, fungicidal control of potato late blight accounts for one-fourth of the total annual expenditure for fungicides on all crops [2]. A tolerance are established for the residue of the fungicide cymoxanil in or on potatoes at 0.05 ppm, and a drinking water level of concern (DWLOCs) for acute exposure to cymoxanil in drinking water was calculated to be 380 ppb [1]. So, cymoxanil as a frequently used fungicide and it has been detected in drinking water [3]. General structure of cymoxanil is shown in Scheme 1.

Pesticides include active ingredients and inert ingredients which may be carcinogens or toxic substances. Prevention of the negative effects of pesticides requires a systematic control of content of their remains in agricultural products, food, fodder, soil, and water [4].

Reliable analytical procedures are therefore needed for their correct determination. In this light, the development of analytical methods to monitor different types of pesticides and pesticides residues in several samples of biological or environmental interest acquires a fundamental importance.

Various instrumental techniques have been developed to study cymoxanil including chromatography [5–11] and spectrophotometry [12]. Also the degradation [13] of cymoxanil especially biodegradation [14] and photocatalytic degradation [15] have been studied. Electroanalytical techniques such as voltammetry, amperometry, and polarography are characterized by simplicity, sensitivity, cost-effectiveness, precision, and accuracy, so they have been used for the determination of pesticides [16, 17]. A review of the literature revealed that no reports have been published on the electrochemical studies of cymoxanil. The aim of this work is to investigate the voltammetric behavior of the cymoxanil, and apply the method for the determination of cymoxanil in commercial formulation and water samples.

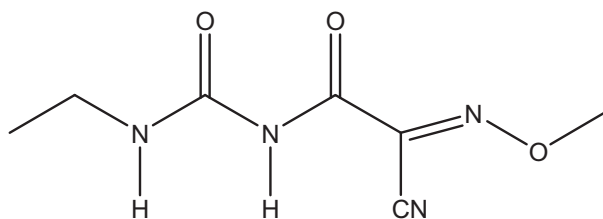
## 2 Experimental

### 2.1 Apparatus

The square-wave voltammograms were obtained with a Bioanalytical Systems-epsilon potentiostat/galvanostat (BAS, West Lafayette, IN,

**Correspondence:** R. İnam, Faculty of Art and Science, Department of Chemistry, Gazi University, 06500 Ankara, Turkey.  
E-mail: rinam@gazi.edu.tr

**Abbreviations:** HMDE, hanging mercury drop electrode; LOD, limit of detection; LOQ, limit of quantification; SWSV, square-wave stripping voltammetry.



**Scheme 1.** The chemical structure of cymoxanil.

USA) analyzer coupled with a BAS-CGME (controlled growth mercury electrode) static mercury drop electrode stand. A three-electrode system was used, consisting of a platinum counter electrode, an Ag/AgCl (3 M NaCl) reference electrode and a hanging mercury drop electrode (HMDE) as a working electrode. All experiments were performed at room temperature. pH was measured with a Hanna HI 8521 (Hanna Instruments, Singapore) pH meter with combined glass electrode. The HPLC system (Agilent 1100 HPLC system, Agilent Technologies, USA) consisted of a quaternary pump, a Rheodyne injector equipped with a 20  $\mu$ L sample loop, 150 mm Zorbax Eclipse XDB C18 5  $\mu$ m column, and a model of L-7455 diode array and multiple wavelength UV-VIS detector (200 nm) controlled by Agilent Chem.

## 2.2 Reagents

Cymoxanil (99% purity) was obtained from Du Pont. Agrochemical formulation Tri-Milttox Max (equivalent to 4.0% m/m of cymoxanil, 13.3% of Mancozeb and 30.0% of copper as copper sulfate) was provided from Sygenta crop Protection AG in Turkey. Cymoxanil stock solutions (200  $\mu$ g/mL) were daily prepared with an exact weight of the pure pesticide in 50% water–acetonitrile solution and kept in the dark in a refrigerator. Supporting electrolyte namely Britton–Robinson buffer (B–R buffer, 0.04 M, pH 3–11) was prepared in doubly distilled water. pH 1.0 and 2.0 were prepared from hydrochloric acid. Working solutions were prepared daily by dilution of the stock solution. Other chemicals used were of analytical reagent grade.

The mercury (proanalysis) was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO<sub>3</sub> and water columns in the form of fine droplets. The collected mercury was dried between sheets of filter paper. Before use, a square-wave voltammogram of this mercury was recorded in order to confirm the absence of impurities.

## 2.3 Square-wave Voltammetric Procedure

The peak current quietly depends on the square-wave voltammetric parameters. In order to obtain the maximum development of the square-wave cathodic stripping peak current, optimization of frequency ( $f$ ), amplitude ( $\Delta E$ ) and staircase step potential ( $\Delta E_s$ ) were attempted. A 10 mL volume of the supporting electrolyte (B–R buffer solution with a pH 7.0) was introduced into voltammetric cell, and then deaerated high-purity nitrogen (99.999%) for about 5 min. The selected accumulation potentials from +200 to –500 mV were applied for various accumulation periods from 0.0 to 50 s under stirring at 400 rpm and nitrogen atmosphere. The stirring was stopped and, after 5 s of equilibrating time, the voltammogram of sample was recorded by applying a negative-going scan.

## 2.4 Formulation Assay Procedure

A suitable amount of fungicide formulation Tri-Milttox Max<sup>®</sup> (4.0% cymoxanil by mass) equivalent to 200  $\mu$ g/mL cymoxanil was accurately prepared in 50% water–acetonitrile, and sonicated 5 min. In the square-wave stripping voltammetry (SWSV) experiments, 10  $\mu$ L of an aliquot of this clear supernatant liquor was added to 10.0 mL of the pH 7.0 solution in the electrochemical cell (previously deaerated for 5 min with humidified, 99.999% ultra-pure nitrogen) and measured under optimum experimental conditions. The cymoxanil in fungicide formulation was analyzed by using the maximum voltammetric peak current obtained at about –670 mV (vs. Ag/AgCl), using the standard addition method.

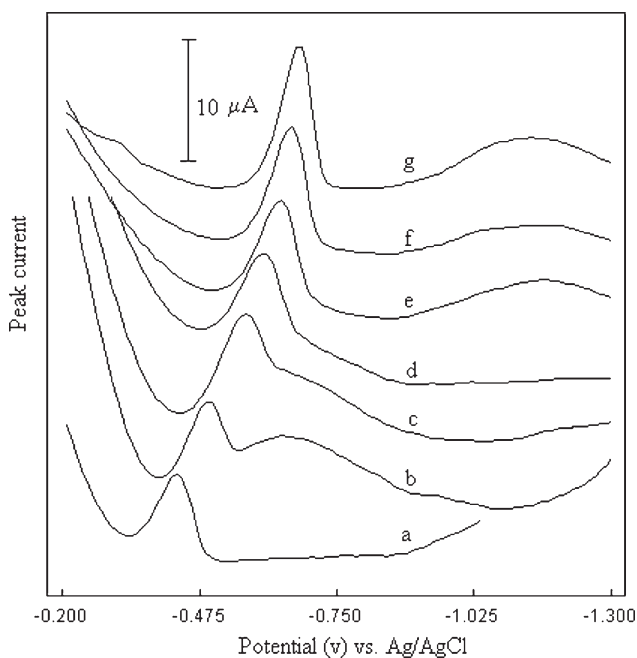
## 3 Result and Discussion

### 3.1 The Voltammetric Behavior of Cymoxanil

#### 3.1.1 Effect of pH

The Britton–Robinson buffer solution (0.04 M) was chosen for its wide pH range applicability. Figure 1 shows typical SWS voltammograms of 200  $\mu$ g/L cymoxanil. The voltammetric reduction of cymoxanil exhibited a single well-defined peak in the pH ranges of 2.0  $\leq$  pH  $\leq$  8.0. Dissociation constant of the fungicide cymoxanil in water was  $pK_a = 9.7 \pm 0.2$  [1]. SWV voltammetric studies showed that, the molecule could not be reducible at pH  $\geq pK_a$ . The dependence  $I_p = f(\text{pH})$  indicates that the reduction process involves the protonated species of the cymoxanil compound. In other word, the non-protonated form was responsible for the disappearing of the limiting currents at pH  $\geq pK_a$  values.

As shown in Fig. 1, the peak potential of the cymoxanil peak was shifted to more negative values with increasing pH, showing a single



**Figure 1.** SWS voltammograms of 200  $\mu$ g/L cymoxanil. (a) pH 2.0, (b) pH 3.0, (c) pH 4.0, (d) pH 5.0, (e) pH 6.0, (f) pH 7.0, and (g) pH 8.0 ( $E_{\text{acc}} = -200$  mV,  $t_{\text{acc}} = 10$  s,  $\Delta E_s = 10$  mV,  $f = 350$  Hz,  $\Delta E = 75$  mV).

linear segment with a slope of 41.4 mV/pH in the pH range of 2.0–8.0. The linear segment can be expressed by following regression equation:

$$E_p(\text{mV}) = -41.4 \text{ pH} - 374.3 \text{ (pH 2.0 – 8.0)} \quad (r = 0.970) \quad (1)$$

A shift of the peak potentials with pH towards more negative value, indicating that the reduction process involves  $\text{H}^+$  coupled with the reduction process. The study of the influence of pH on peak currents was also evaluated to obtain the optimum pH for maximum signal. The highest intensity found at a pH 8.0. Cymoxanil hydrolyzes under aqueous conditions at neutral and especially alkaline pHs. Hydrolysis constant of cymoxanil at pH 7.0 was 34 h and at pH 9.0 was 31 min [1], so pH 7.0 was chosen as an optimum pH for further analytical studies.

### 3.1.2 Optimizing Parameters

The influence of accumulation potential on the peak current of cymoxanil was examined over the potential range of +200 to –500 mV in B–R buffer of pH 7.0. An accumulation potential of –400 mV was chosen and used throughout the study due to the well-defined and sensitive features of the cymoxanil peak (Fig. 2a). The dependence of the SWS voltammetric peak current of 100  $\mu\text{g/L}$  cymoxanil on the preconcentration time (from 0 to 50 s) at  $E_{\text{acc}} = -400 \text{ mV}$  was studied (Fig. 2b). The maximum peak current was obtained at an accumulation time of 10 s.

The influence of the frequency and pulse amplitude were studied within 25–400 Hz and 5–200 mV, respectively. Peak intensities increased with frequency until 350 Hz. The half peak width increased also resulting in distortion of the current response for higher frequencies and therefore 350 Hz was chosen as an optimal frequency. For analytical applications, pulse amplitude of 75 mV was suitable due to its higher sensitivity.

### 3.1.3 Cyclic Voltammetry

The cyclic voltammetric measurements performed with 8.0 mg/L cymoxanil, showed an irreversible nature of the reduction wave at the hanging mercury electrode in the range of scan rates comprised between 5 and 4000 mV/s at pH 7 B–R buffer (Fig. 3). Scan rate studies were then carried out to assess whether the processes were under diffusion or adsorption controlling. When scan rate was varied from 5 to 4000 mV/s, a linear relationship was observed

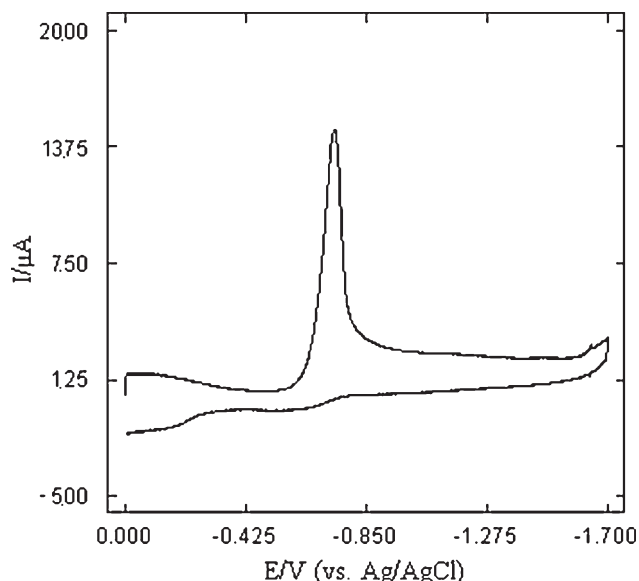


Figure 3. Cyclic voltammogram of 8.0 mg/L cymoxanil.

between the peak intensity and square root of scan rate, demonstrating that the phenomenon was diffusion controlled.

$$I_p (\mu\text{A}) = 0.559 \nu^{1/2} (\text{m/Vs}^{-1})^{1/2} - 2.753 \quad (r = 0.996) \quad (2)$$

A plot of logarithm of peak current versus logarithm of scan rate gave a straight line with a slope of 0.64 very close to the theoretical value of 0.5, which is expressed for an ideal reaction for the diffusion-controlled electrode process [18]. The equation was

$$\log I_p (\mu\text{A}) = 0.6431 \log \nu (\text{m/Vs}^{-1}) - 0.7857 \quad (r = 0.999) \quad (3)$$

As can be seen from Fig. 3, no anodic peak was observed on the measured cyclic voltammogram. On the other hand, the observed peak potential shifted to more negative values with the increase of scan rate. These observations indicated the irreversibility nature of the cathodic reduction process. Considering the pH dependence on the reduction process ( $\text{H}^+$  coupled with the reduction process) and cyclic voltammetric studies, the possible mechanism for the reduction of cymoxanil could be proposed as follows (Scheme 2).

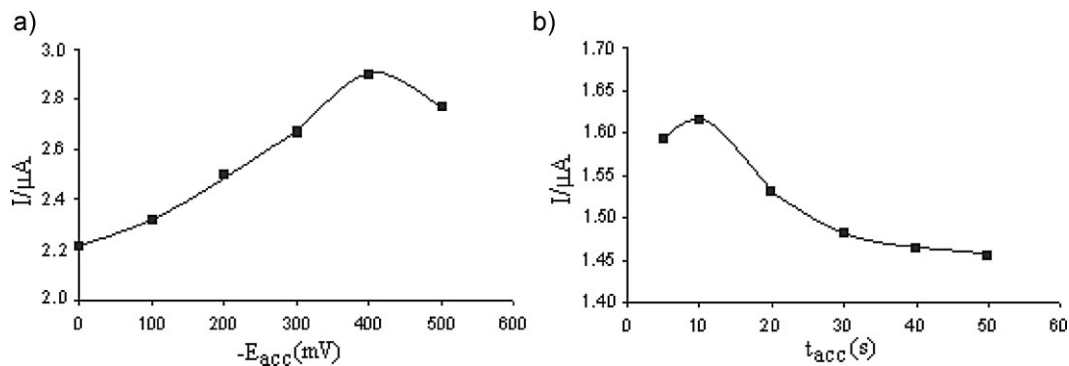
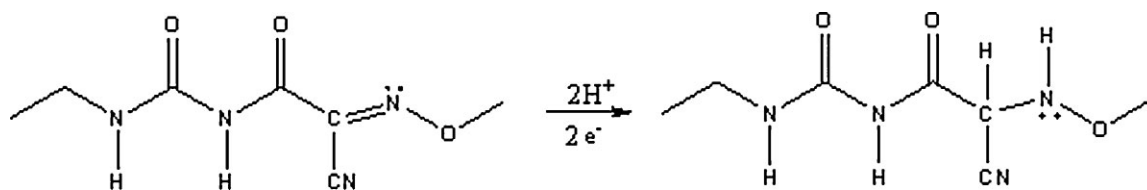


Figure 2. (a) Effect of accumulation potential ( $E_{\text{acc}}$ ) and (b) accumulation time on the cathodic adsorptive peak current response for 100  $\mu\text{g/L}$  cymoxanil in B–R buffer at pH 7.0.



**Scheme 2.** Possible mechanism for the reduction of cymoxanil.

### 3.2 Analytical Applications

The influence of pH and voltammetric parameters exhibited the optimum conditions; pH 7.0 B-R buffer solution, an accumulation potential  $-400$  mV, a reduction peak potential of  $-680$  mV (vs. Ag/AgCl), accumulation time of 10 s, pulse amplitude of 75 mV with frequency of 350 Hz at an ambient temperature of  $20 \pm 3^\circ\text{C}$ . Under these experimental conditions, a calibration curve was plotted using the standard additions of cymoxanil to the  $0.04 \text{ mol/L}^{-1}$  B-R buffer (pH 7.0). The obtained SWS voltammetric responses were displayed in Fig. 4. A linear relationship between the peak current of cymoxanil versus concentration can be established in the range of  $23.6$ – $1950 \mu\text{g/L}$  with the analytical equation given by:

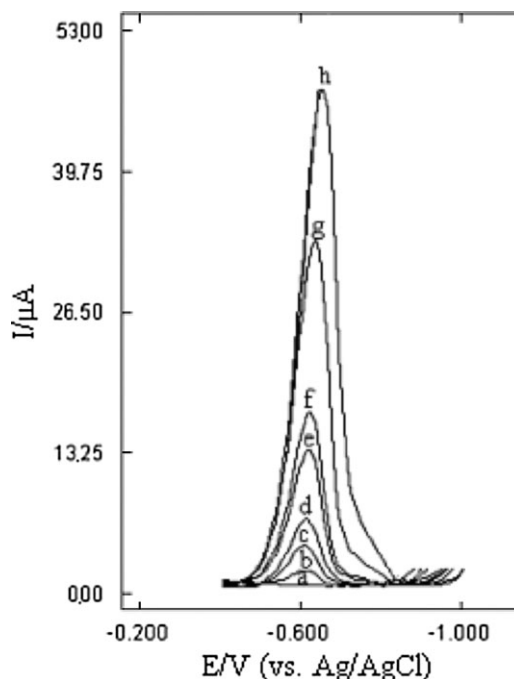
$$I_p (\mu\text{A}) = 0.0174 C (\mu\text{g/L}) + 0.9482 \quad (4)$$

The limit of detection (LOD) and limit of quantification (LOQ) were obtained as  $7.1$  and  $23.6 \mu\text{g/L}$ , respectively, according to the relation  $k \text{ SD}/b$  (where  $k = 3$  for LOD and  $k = 10$  for LOQ, SD is the standard deviation of the fortified blank ( $10 \mu\text{g/L}$ ), and  $b$  is the slope of the calibration curve) [19]. The regression equations associated with the calibration curves (Tab. 1) exhibited good linearity ( $r = 0.998$ ) that supported the validation of the proposed procedure.

The applicability and validation of the proposed SWS voltammetric method for the assay of cymoxanil in spiked water samples and agricultural dosages were investigated. The accuracy of the developed method was checked by calculating the recovery of cymoxanil from the water samples and agrochemical pesticide formulation Tri-Milttox Max<sup>®</sup>.

Using the optimal conditions, calibration curves were constructed for cymoxanil in river water sample. Square-wave voltammograms obtained from the standard addition of cymoxanil in river water were presented in Fig. 5. The peak currents were linearly related to the pesticide concentration between  $23.2$  and  $1600 \mu\text{g/L}$ , with the analytical equation given by

$$I_p (\mu\text{A}) = 0.0132 C (\mu\text{g/L}) + 0.0374 \quad (r = 0.998) \quad (5)$$



**Figure 4.** Square-wave voltammograms obtained from standard addition of cymoxanil. (a) 10.0 mL blank (pH 7.0, B-R buffer), (b)  $10 \mu\text{g/L}$  cymoxanil, (c)  $20 \mu\text{g/L}$  cymoxanil, (d)  $100 \mu\text{g/L}$  cymoxanil, (e)  $400 \mu\text{g/L}$  cymoxanil, (f)  $600 \mu\text{g/L}$  cymoxanil, (g)  $800 \mu\text{g/L}$  cymoxanil, and (h)  $1000 \mu\text{g/L}$  cymoxanil.

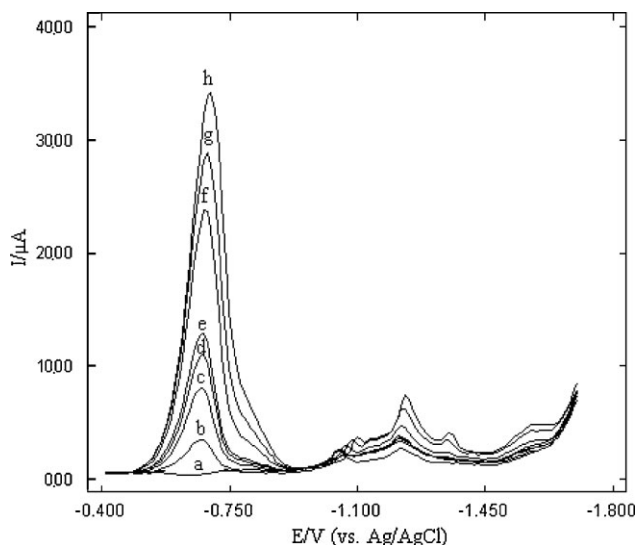
The LOD and LOQ were obtained as  $6.9$  and  $23.2 \mu\text{g/L}$ , respectively. The regression equations associated with the calibration curve (Tab. 1) exhibited good linearity ( $r = 0.998$ ) that supported the validation of the proposed procedure.

The validity of the proposed method was further proven by spiking with cymoxanil in river water samples obtained from Kızılırmak River, Turkey. For this purpose, 10.0 mL of river water was spiked

**Table 1.** Statistical parameters for the SW voltammetric determination of cymoxanil.

Parameter	B-R buffer solution <sup>a)</sup>	River water	Tap water
Measured potential (mV)	$-680$	$-670$	$-650$
Linearity range ( $\mu\text{g/L}$ )	$23.6$ – $1950$	$23.2$ – $1600$	$18.7$ – $2000$
Slope ( $\mu\text{A}/\mu\text{g/L}$ )	$0.0174$	$0.0132$	$0.0136$
Intercept ( $\mu\text{A}$ )	$0.9482$	$0.0374$	$0.1057$
Correlation coefficient	$0.998$	$0.998$	$0.999$
LOD ( $\mu\text{g/L}$ )	$7.1$	$6.9$	$5.5$
LOQ ( $\mu\text{g/L}$ )	$23.6$	$23.2$	$18.7$
Repeatability of peak potential (RSD%)	$0.74$	$0.76$	$1.29$
Repeatability of peak current (RSD%)	$1.55$	$1.15$	$1.53$

<sup>a)</sup> B-R: Britton–Robinson buffer solution (pH 7.0).



**Figure 5.** Square-wave voltammograms obtained from standard addition of cymoxanil in river water. (a) Blank (7 mL pH 7.0 + 3 mL river water), (b) 10  $\mu\text{g/L}$  cymoxanil, (c) 20  $\mu\text{g/L}$  cymoxanil, (d) 100  $\mu\text{g/L}$  cymoxanil, (e) 400  $\mu\text{g/L}$  cymoxanil, (f) 600  $\mu\text{g/L}$  cymoxanil, (g) 800  $\mu\text{g/L}$  cymoxanil, and (h) 1000  $\mu\text{g/L}$  cymoxanil.

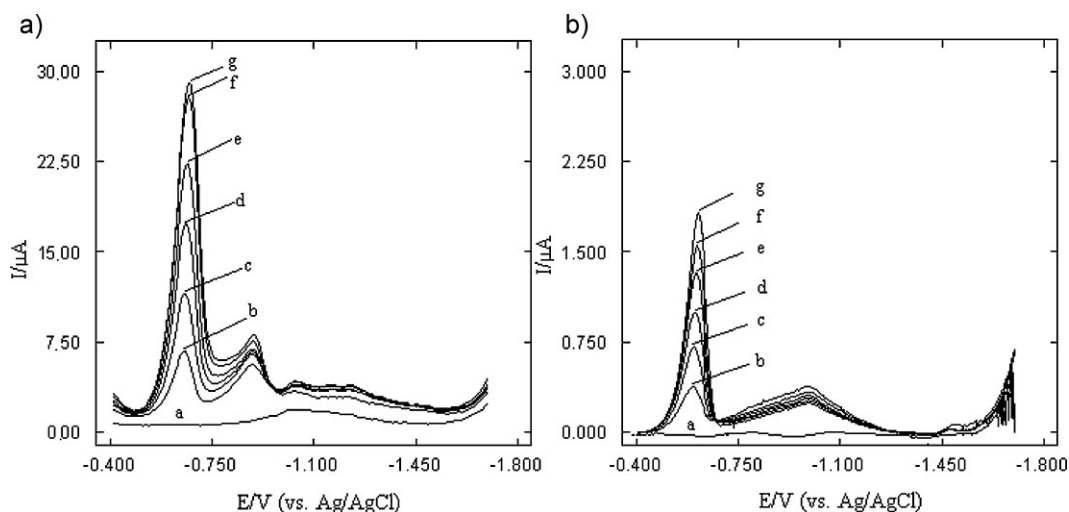
with 400–2000  $\mu\text{g/L}$  cymoxanil solutions. After homogenizing the samples in Erlenmeyer flasks, they were placed in a temperature-controlled water-bath and shaken for 30 min at an ambient temperature. From the supernatant, 1.0 mL of aliquots was transferred to the voltammetric cell containing 9.0 mL of B-R buffer solution with a pH of 7.0. The fungicide was determined from the peak current generated at about  $-670$  mV (vs. Ag/AgCl), using multiple standard additions. For tap water analysis, 10.0 mL of the samples were spiked with cymoxanil stock solutions at different concentrations. After repeating the above procedure, the fungicide in spiked tap water was detected by multiple standard addition using the peak appeared at  $-680$  mV (vs. Ag/AgCl). Tab. 2 shows the experimental results corresponding to spiked cymoxanil in river and tap water samples. Recoveries calculated for river and tap water samples spiked with 40  $\mu\text{g/L}$  level were  $40.2 \pm 0.8$  and  $39.8 \pm 0.9$   $\mu\text{g/L}$  at 95% confidence level, respectively. The sufficiently good recoveries and low relative standard deviations reflect the high accuracy and precision of the proposed square-wave voltammetric method.

The optimized procedure was also successfully applied for determination of cymoxanil in commercial formulation Tri-Milttox Max<sup>®</sup>. The amount of cymoxanil in commercial formulation was determined by the standard addition method based on the average of four replicate measurements using a proposed voltammetric method and differential pulse polarography (Fig. 6). The obtained results were also compared with those obtained by HPLC method.

**Table 2.** The recoveries of the cymoxanil from river and tap water samples.

Added ( $\mu\text{g/L}$ )	Found <sup>a)</sup> ( $\mu\text{g/L}$ ) $\{\bar{X} \pm \frac{t_s}{\sqrt{n}}\}$		Recovery <sup>a)</sup> (%) $\{\bar{X} \pm \frac{t_s}{\sqrt{n}}\}$	
	River	Tap water	River	Tap water
0.0	ND	ND	ND	ND
40.0	$40.2 \pm 0.8$	$39.8 \pm 0.9$	$100.4 \pm 2.0$	$99.5 \pm 2.3$
100.0	$101.0 \pm 2.5$	$101.3 \pm 0.4$	$101.0 \pm 2.5$	$101.3 \pm 0.4$
200.0	$200.0 \pm 1.5$	$201.2 \pm 2.8$	$100.0 \pm 3.8$	$100.6 \pm 1.4$

<sup>a)</sup>  $t = 95\%$  confidence level,  $n = 4$ . ND, not detected.



**Figure 6.** (a) SWS voltammograms for the determination of cymoxanil in agrochemical pesticide Tri-Milttox Max<sup>®</sup> at pH 7.0. a, 10 mL blank; b, Tri-Milttox Max<sup>®</sup> containing 100  $\mu\text{g/L}$  cymoxanil; c, b + 100  $\mu\text{g/L}$  cymoxanil; d, c + 100  $\mu\text{g/L}$  cymoxanil; e, d + 100  $\mu\text{g/L}$  cymoxanil; f, e + 100  $\mu\text{g/L}$  standard cymoxanil; g, f + 100  $\mu\text{g/L}$  standard cymoxanil. (b) DP polarograms obtained for the determination of cymoxanil in agrochemical pesticide Tri-Milttox Max<sup>®</sup> at pH 7.0. a, 10 mL blank; b, Tri-Milttox Max<sup>®</sup> containing 100  $\mu\text{g/L}$  cymoxanil; c, b + 100  $\mu\text{g/L}$  cymoxanil; d, c + 100  $\mu\text{g/L}$  cymoxanil; e, d + 100  $\mu\text{g/L}$  cymoxanil; f, e + 100  $\mu\text{g/L}$  cymoxanil; g, f + 100  $\mu\text{g/L}$  cymoxanil.

**Table 3.** Assay results from agrochemical pesticide formulation Tri-Milttox Max<sup>®</sup>.

	SWSV	HPLC
Labeled claim (% m/m)	4.00	4.00
Amount found (% m/m)	4.10 ± 0.30	4.12 ± 0.06
RSD (%)	7.30	1.46
Bias (%)	+2.5	+3.0
Student's <i>t</i> -test	0.12 [2.57] <sup>a)</sup>	
Variance ratio <i>F</i> -test	16.88 [19.6] <sup>a)</sup>	

<sup>a)</sup> The figures in parenthesis are the tabulated values of *t* and *F* at 95% confidence level (*n* = 4 for SWSV and *n* = 3 HPLC).

Statistical analysis of the results by both methods using the student's *t*-test and variance ratio *F*-test, show no significant difference between the performance of the two methods regarding the accuracy and precision, respectively (Tab. 3).

### 3.3 Influences of Co-Existing Species

The influence of some inorganic species and pesticides on the SW voltammetric determination of cymoxanil was investigated. The interference studies were performed using the various interfering species, mostly electroactive. The degree of interference effects were shown as the ratio of the peak currents in the presence of the interfering ions to that in their absence (by percentage). The co-existing species taken as one to 100 times the amount of cymoxanil had no serious interfering effects on the target molecule, with the exception of anilazine. The results for the recoveries in the presence of co-existing species were summarized in Tab. 4.

**Table 4.** The influence of some co-existing species on the SW voltammetric determination of cymoxanil (20 µg/L).

Interfering species	Fold	Recovery (%) <sup>a)</sup> $\bar{X} \pm \frac{tS}{\sqrt{n}}$	Interfering species	Fold	Recovery (%) <sup>a)</sup> $\bar{X} \pm \frac{tS}{\sqrt{n}}$
Ni <sup>2+</sup>	1	100.4 ± 2.2	NH <sub>4</sub> <sup>+</sup>	1	101.6 ± 3.8
	10	101.6 ± 1.1		10	100.3 ± 1.4
	100	101.1 ± 2.1		100	99.7 ± 1.5
Co <sup>2+</sup>	1	100.4 ± 2.2	NO <sub>3</sub> <sup>-</sup>	1	101.0 ± 1.5
	10	100.8 ± 1.7		10	100.2 ± 1.1
	100	98.3 ± 3.2		100	99.9 ± 2.1
Zn <sup>2+</sup>	1	102.3 ± 1.6	Na <sup>+</sup>	1	100.4 ± 1.2
	10	100.3 ± 0.8		10	99.7 ± 0.6
	100	99.2 ± 1.2		100	100.4 ± 1.7
K <sup>+</sup>	1	99.3 ± 0.4	Cu <sup>2+</sup>	1	99.3 ± 1.5
	10	100.4 ± 0.3		10	100.4 ± 1.8
	100	100.6 ± 1.8		100	95.1 ± 3.5
Pb <sup>2+</sup>	1	101.1 ± 0.8	Mg <sup>2+</sup>	1	100.3 ± 0.8
	10	100.0 ± 1.7		10	102.1 ± 0.9
	100	99.3 ± 1.3		100	101.9 ± 1.7
Cl <sup>-</sup>	1	99.8 ± 1.7	CN <sup>-</sup>	1	95.1 ± 1.1
	10	97.1 ± 5.8		10	86.9 ± 5.7
	100	99.4 ± 3.7		100	91.1 ± 4.5
Cyromazine	1	91.42	Anilazine	1	83.52
	2	86.72		2	71.05
Acifluorfen	1	92.10	Alanycarb	1	94.89
	2	80.20		2	86.89

<sup>a)</sup> *t* = 95% confidence level, *n* = 4.

## 4 Conclusion

A novel electroanalytical method involving SWSV at hanging mercury electrode was proposed to determine cymoxanil content in agrochemical formulation and water samples. The SWS voltammetric method presented for the quantitative determination of cymoxanil allowed the accurate determination and was found to be rapid, simple, and highly sensitive. The main advantage of such a procedure is the possibility to determine the concentration of the active component directly from the fungicide formulation and water samples without any previous treatment, such as extraction, clean-up, derivatization, or pre-concentration which are tedious, time consuming, and also polluting. The present method could possibly be applied for the determination of cymoxanil in environmental samples as well as for quality control laboratories.

The authors have declared no conflict of interest.

## References

- [1] Environmental Protection Agency, EPA, *Cymoxanil Pesticide Fact Sheet*, PN EPA, Washington, DC 1998.
- [2] D. C. Erwin, O. K. Ribeiro, (Eds.), Introduction to the Genus *Phytophthora*, in: *Phytophthora Diseases Worldwide*, American phytopathological society press, St. Paul, MN, USA 1996.
- [3] P. Fidente, C. Di Giovanni, S. Seccia, P. Morrica, Determination of Cymoxanil in Drinking Water and Soil Using High-performance Liquid Chromatography, *Biomed. Chromatogr.* **2005**, *19* (10), 766.
- [4] M. S. Ibrahim, K. M. Al-Magboul, M. M. Kamal, Voltammetric Determination of the Insecticide Buprofezin in Soil and Water, *Anal. Chim. Acta* **2001**, *432* (1), 21.
- [5] O. L. D. Sabando, Z. G. D. Balugera, M. A. Goicolea, E. Rodriguez, M. C. Sampedro, R. J. Barrio, Determination of Simazine and Cymoxanil in Soils by Microwave-assisted Solvent Extraction and HPLC with Reductive Amperometrical Detection, *Chromatographia* **2002**, *55* (11–12), 667.
- [6] M. J. Hengel, M. Miller, Analysis of Pesticides in Dried Hops by Liquid Chromatography-Tandem Mass Spectrometry, *J. Agric. Food Chem.* **2008**, *56* (16), 6851.
- [7] A. M. Rodrigues, V. Ferreira, V. V. Cardoso, E. Ferreira, M. J. Benoliel, Determination of Several Pesticides in Water by Solid-phase Extraction, Liquid Chromatography and Electrospray Tandem Mass Spectrometry, *J. Chromatogr. A* **2007**, *1150* (1–2), 267.
- [8] P. Morrica, P. Fidente, S. Seccia, High-performance Liquid Chromatographic Mass Spectrometric Identification of the Photoproducts of Cymoxanil, *Biomed. Chromatogr.* **2005**, *19* (7), 506.
- [9] A. C. Martel, M. Porthault, Pesticide Residues in Raspberries and Lettuce: Extraction and Comparison of Three Chromatographic Methods: HPLC, HPTLC and GC, *J. Liq. Chromatogr. Relat. Technol.* **2000**, *23* (19), 3043.
- [10] F. Tellier, R. Fritz, P. Leroux, A. C. Sinclair, J. C. Cherton, Metabolism of Cymoxanil and Analogs in Strains of the Fungus *Botrytis cinerea* Using High-performance Liquid Chromatography and Ion-pair High-performance Thin-layer Chromatography, *J. Chromatogr. B* **2002**, *769* (1), 35.
- [11] M. J. Hengel, T. Shibamoto, Development of a Gas Chromatographic Method for Fungicide Cymoxanil Analysis in Dried Hops, *J. Agric. Food Chem.* **2001**, *49* (2), 570.
- [12] V. Feigenbrugel, S. Le-Calv'e, P. M. Mirabel, Molar Absorptivities of 2,4-D, Cymoxanil, Fenpropidin, Isoproturon and Pyrimethanil in Aqueous Solution in the Near-UV, *Spectrochim. Acta Part A* **2006**, *63* (1), 103.
- [13] P. Morrica, S. Traube, J. J. Anderson, S. Lawler, S. Seccia, P. Fidente, R. S. Swain, S. L. Mattson, Kinetics and Mechanism of Cymoxanil Degradation in Buffer Solutions, *J. Agric. Food Chem.* **2004**, *52* (1), 99.

- [14] A. S. Derbalah, E. B. Belal, Biodegradation Kinetics of Cymoxanil in Aquatic System, *Chem. Ecol.* **2008**, 24 (3), 169.
- [15] I. Oller, W. Gernjak, M. I. Maldonado, L. A. Pérez-Estrada, J. A. Sánchez-Pérez, S. Malato, Solar Photocatalytic Degradation of Some Hazardous Water-soluble Pesticides at Pilot-plant Scale, *J. Hazard. Mater.* **2006**, 138 (3), 507.
- [16] R. İnam, T. Sarigul, E. Z. Gülerman, N. Uncu, Polarographic Determination of Herbicide Thifensulfuron Methyl/Application to Agrochemical Pesticide, Soil, and Fruit Juice, *Int. J. Environ. Anal. Chem.* **2006**, 86 (15), 1135.
- [17] P. Qiu, Y. N. Ni, Determination of Ziram in Vegetable Samples by Square Wave Voltammetry, *Chin. Chem. Lett.* **2008**, 19 (11), 1337.
- [18] E. Laviron, L. Roullier, C. J. Degrand, A Multilayer Model for the Study of Space Distributed Redox Modified Electrodes 2. Theory and Application of Linear Potential Sweep Voltammetry for a Simple Reaction, *J. Electroanal. Chem.* **1980**, 112 (1), 11.
- [19] L. A. Currie, International Recommendations Offered on Analytical Detection and Quantification Concepts and Nomenclature, *Anal. Chim. Acta* **1999**, 391 (2), 103.