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Electrochemistry

SQUARE WAVE ADSORPTIVE STRIPPING VOLTAMMETRIC DETERMINATION OF CYROMAZINE INSECTICIDE WITH MULTI-WALLED CARBON NANOTUBE PASTE ELECTRODE

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The electrochemical behavior of cyromazine (N-cyclopropyl-1,3,5-triazine-2,4,6 triamine) insecticide has been studied at newly prepared multi-wall carbon nanotubes paste electrodes using square wave stripping voltammetry. The cyromazine was accumulated at 0.0 mV [vs. Ag/AgCl (3 M NaCl)] and a well-defined anodic peak obtained at +1110 mV in 0.1 M H_2SO_4. The cyclic voltammetric measurements showed an irreversible nature of oxidation wave in the range of scan rates comprised between 500 and 4000 mV s^{-1}. The calibration curve obtained from square wave stripping voltammetry was linear in the range 0.41 to 83.30 µg/mL with a detection limit of 0.12 µg/mL. The method was applied to the direct determination of cyromazine in natural water samples. Recoveries calculated for river and tap water samples spiked with 10.0 µg/mL level were 101.5 ± 1.9% and 100.6 ± 2.3% at 95% confidence level, respectively. The method was extended to the determination of cyromazine in agrochemical formulation Trigard® with a recovery of 100.49% and accuracy was in agreement with that obtained by HPLC comparison method. Influences of some interfering ions and pesticides were also investigated.

Keywords: Carbon nanotube paste electrode; Cyclic voltammetry; Cyromazine; Environmental analysis; Square wave stripping voltammetry

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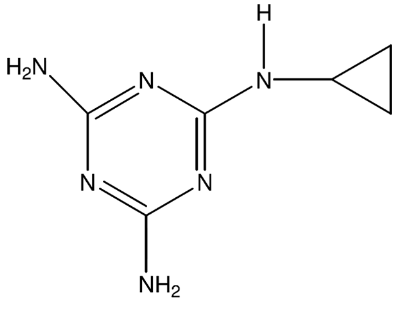
INTRODUCTION

Pesticides include active ingredients and inert ingredients that may be carcinogens or toxic substances. Cyromazine is a triazine group pesticide used for fly control in cattle manure, field crops, fruits, and vegetables by inhibiting insect growth, especially Diptera (Thomson 1994). It is slightly toxic by ingestion, with informed oral LD_{50} values of 3387 mg^{-1} kg in rats (EPA 2000). Tolerances are established for the residue of the insecticide cyromazine in potatoes at 0.8 ppm, in corn at 0.5 ppm level (EPA 1999). The structure of cyromazine (N-cyclopropyl-1,3,5-triazine-2,4,6 triamine) is shown in Scheme 1.

Prevention of the negative effects of pesticides requires a systematic control of content of their remains in agricultural products, food, fodder, soil, and water (Ibrahim, Al-Magboul, and Kamal 2001). Reliable analytical procedures are, therefore, needed for their determination. As a result, the development of analytical methods to monitor different types of pesticides and pesticides residues in biological or environmental samples is fundamentally important. In the literature, the determination of cyromazine has been carried out by different instrumental techniques such as chromatography (Chou, Hwang, and Lee 2003; Qian et al. 2009; Sancho et al. 2005; Wei et al. 2009; Yokley et al. 2000, 1998; Zhang et al. 2009) or Raman spectrophotometry (Sergio et al. 2004). Capillary electrophoresis (Blasco, Pico, and Andreu 2009; Hernandez et al. 2004, 2005) and photocatalytic degradation (Goutailler et al. 2001) have also been studied. Electroanalytical techniques such as voltammetry, amperometry, and polarography are characterized by simplicity, sensitivity, cost-effectiveness, precision, and accuracy; as a result, they have been used for the determination of pesticides (Qiu and Ni 2008; Sarıgül and İnam 2009).

Carbon nanotubes have been used for the determination of a variety of species such as drugs and pesticides (Goyal and Bishnoi 2009; Hedge, Shetti, and Nandibewoor 2009; Jiang et al. 2009; Wang and Fan 2009; C. Yang et al. 2008; Q. J. Yang et al. 2009). They can dramatically improve the electrochemical responses of biomolecules due to the large specific area, unique architecture, and remarkable mechanical and electrical properties. The subtle electronic properties suggest that they have the ability to promote charge-transfer reactions when used as an electrode. Their application as analytical sensors has been documented to result in low detection limits, high sensitivities, reduction of overpotentials, and resistance to surface fouling.

In the present work, the prepared multiwall carbon nano tubes paste (MWCNTPEs) electrodes are used for the square wave stripping voltammetric (SWSV)



Scheme 1. The chemical structure of cyromazine.

determination of cyromazine. To the best of our knowledge, there is no report on using multiwall carbon nanotubes for determination of cyromazine. The method is extended to determination of cyromazine in agrochemical formulation Trigard® and natural waters. The sufficiently good recoveries, HPLC comparison results, and low relative standard deviations reflect the high accuracy and precision of the proposed voltammetric method. The influences of some interfering species will also be investigated.

EXPERIMENTAL

Apparatus

The square wave voltammograms were obtained with a Bioanalytical Systems-Epsilon potentiostat/galvanostat (BAS, West Lafayette, IN, USA) analyzer coupled with a BAS-C3 cell stand. A three-electrode system was used, consisting of a platinum counter electrode, an Ag/AgCl (3 M NaCl) reference electrode, and a multiwall carbon nanotube paste electrode (MWCNTPE) as a working electrode. All experiments were performed at room temperature. The 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 µL sample loop, 150 mm Zorbax Eclipse XDB C18 (150 mm x 4.6 mm, id, 5 µm) column, and a model of L-7455 diode array and multiple wavelength UV–vis detector (200 nm) controlled by Agilent Chem workstation.

The MWCNTPE was prepared by mixing 15% multiwall carbon nano tube powder (Sigma Aldrich, Inc) with 85% mineral oil. The mixture was homogenized and the mixed paste was then inserted in a plastic syringe needle using a 3-mm diameter copper wire that was connected to the system.

Reagents

Cyromazine (99.0% purity) was obtained from Du Pont. Agrochemical formulation Trigard® (equivalent to 75.0% m/m of cyromazine) was provided from Syngenta Crop Protection AG in Turkey. Cyromazine stock solutions (400 µg/mL) were daily prepared with an exact weight of the pure pesticide in 100% water 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. The H_2SO_4 of 0.1 M and 0.01 M was used as the electrolyte. Working solutions were prepared daily by dilution of the stock solution. Other chemicals used were of analytical reagent grade.

Square Wave Stripping Voltammetric Procedure

The peak current quietly depends on the square wave voltammetric parameters. In order to obtain the maximum development of the square-wave anodic stripping peak current, optimization of frequency (f), amplitude (ΔE), and staircase step potential (ΔE_s) were attempted. A 10.0 mL volume of the supporting electrolyte (0.1 M H_2SO_4) was introduced into voltammetric cell. The selected accumulation potentials from −200 mV to +1500 mV were applied for various accumulation periods from 0.0

to 150 s under stirring at 400 rpm. The stirring was stopped and, after 5 s of equilibrating time, the voltammogram of sample was recorded by applying a positive-going scan.

Formulation Assay Procedure

A suitable amount of insecticide formulation Trigard® (75.0% cyromazine by mass) equivalent to 400 µg/mL cyromazine was accurately prepared in 100% water and sonicated 5 minutes. In the square wave stripping voltammetric (SWSV) experiments, an aliquot containing 10 µg/mL cyromazine of this clear supernatant liquor was added to 0.1 M H_2SO_4 solution in the electrochemical cell and measured under optimum experimental conditions. Cyromazine in agrochemical formulation was analyzed by using the maximum voltammetric peak current obtained at about +1110 mV vs. Ag/AgCl (3 M NaCl), using the standard addition method.

RESULT AND DISCUSSION

Cyclic Voltammetry

In order to understand the oxidation process of cyromazine on MWCNTPE, cyclic voltammetric study was performed. For this purpose, the cyclic voltammograms of 40 µg/mL cyromazine was investigated on MWCNTPE with different scan rates. As shown in Figure 1, cyclic voltammogram of cyromazine in 0.1 M H_2SO_4 exhibited an anodic peak at about +1050 mV (Ag/AgCl, 3 M NaCl), and no peak was

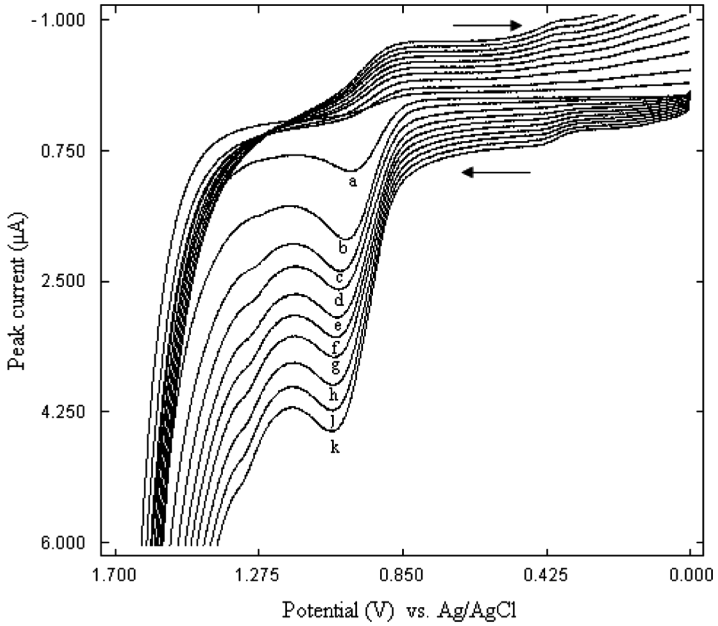


Figure 1. Cyclic voltammogram of 40 µg mL^{-1} cyromazine at MWCNTPE a) 25 mV/s, b) 100 mV/s, c) 200 mV/s, d) 300 mV/s, e) 400 mV/s, f) 500 mV/s, g) 600 mV/s, h) 700 mV/s, j) 800 mV/s, and k) 900 mV/s.

observed on the cathodic direction. This process indicates that the main oxidation peak of cyromazine is irreversible.

The effect of scan rate on the peak potentials and currents was evaluated. Scan rate studies are important to decide whether the electrode process is under diffusion or adsorption control. The oxidation peak currents were linearly dependent on square root of scan rates from 500 to 4000 and 1000–10000 mVs^{-1}.

A plot of logarithm of peak current vs. logarithm of scan rate gave a straight line with a slope of 0.84 very close to the theoretical value of 1.0, which is expressed for an ideal reaction for the adsorption-controlled electrode process (Laviron, Roullier, and Degrand 1980).

$$\log i_p(\mu A) = 0.76 \log (mVs^{-1}) - 0.99 \quad r = 0.989 \ (500-4000\,mVs^{-1}) \tag{1}$$

$$\log i_p(\mu A) = 0.84 \log (mVs^{-1}) - 1.27 \quad r = 0.995 \ (1000-10000\,mVs^{-1}) \tag{2}$$

The peak potential shifted to less positive values (vs. Ag/AgCl, 3 M NaCl) with the increase of scan rate, which confirmed the irreversibility of the oxidation process.

Effect of pH

Cyromazine was oxidized in a wide range of from pH 1.0 to 8.0. As shown Figure 2, square wave stripping voltammetry of cyromazine in different pH solutions showed that the oxidation peak current and potential depended strongly on the solution pH (0.1 and 0.01 M H_2SO_4 and B-R buffer between pH 2.0 and 8.0). The oxidation peak potentials shifted to less positive direction (vs. Ag/AgCl, 3 M NaCl) up to $pH \approx 5.0$ ($pK_a = 5.22$) whereas the positive potential shift were observed in neutral or slightly basic pH's.

As shown Figure 3, the oxidation peak was shifted to less positive values (vs. Ag/AgCl, 3 M NaCl) with increasing pH, showing a two linear segment with a slope of −54.0 mV/pH in the pH range of 2.0 to 6.0 and 22.5 mV/pH in the pH range of 6.0 to 8.0. The intersection point observed at pH 5.5 which corresponds to the $pKa \pm 1$ value of cyromazine ($pKa = 5.22$). The linear segments can be expressed by following regression equations:

$$E_p \ (mV) = -54.0 \ pH \ + 1261.5 \ (pH \ 2.0-5.0) \quad (r = 0.998) \tag{3}$$

$$E_p \ (mV) = 22.5 \ pH - 842.5 \ (pH \ 6.0-8.0) \quad (r = 0.982) \tag{4}$$

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 0.1 M H_2SO_4 solution was chosen as an optimum pH for analytical determination of cyromazine.

Effects of the Accumulation Potential and Accumulation Time

The first parameter to be optimized for the determination 20 μg/mL cyromazine was accumulation potential. The dependence of the stripping peak current on the accumulation potential (E_{acc}) was studied over the range −200 to +1500 mV

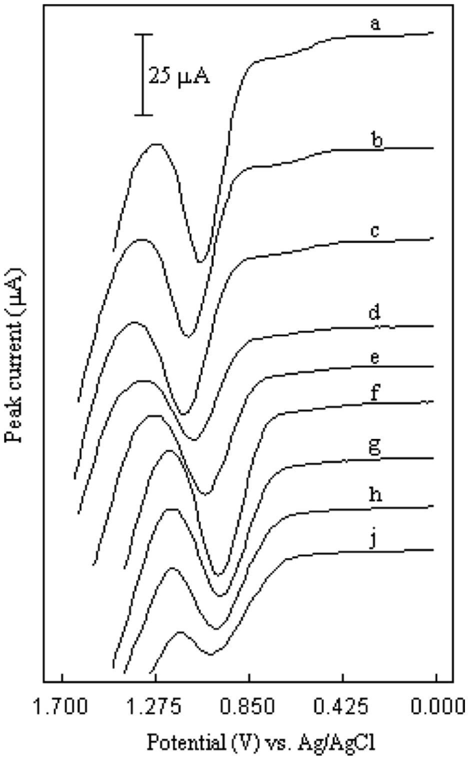


Figure 2. Square wave voltammograms of 50 μg/mL cyromazine as a function of pH. a) 0.1 M H_2SO_4, b) 0.01 M H_2SO_4, c) pH 2.0 B-R buffer, d) pH 3.0 B-R buffer, e) pH 4.0 B-R buffer, f) pH 5.0 B-R buffer, g) pH 6.0 B-R buffer, h) pH 7.0 B-R buffer, and j) pH 8.0 B-R buffer.

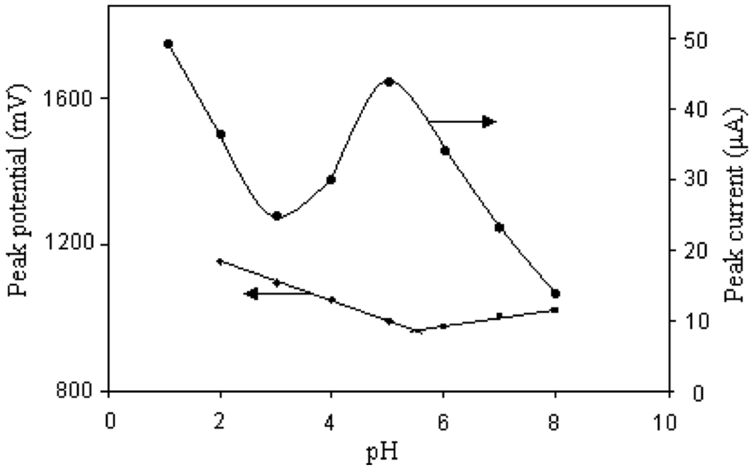


Figure 3. Variation of peak potential and peak current as a function of pH obtained from voltammograms presented in Fig. 2. (→; shows that peak current as a function of pH and ←; shows that peak potential as a function of pH).

Table 1. Optimum operation parameters selected for the determination of cyromazine by SWSV using CNTPE

Parameters/Unit	Optimized values
Accumulation potential/mV	0.0
Accumulation time/s	100
Frequency (Hz)	75
Puls amplitude/mV	100
Step potential/mV	15
Supporting electrolyte	pH $\approx$ 1.0 (0.1 M H_2SO_4)
Peak potential/mV	+1110
Rest time/s	5

and highest peak intensity was obtained at Eacc of 0.0 mV. The dependence of peak current on accumulation time (t_{acc}) at 20 μg/mL of cyromazine was also studied. A gradual increase in peak current intensity was observed between 0 and 100 s starting to decrease in a roughly linear manner, probably due to the saturation of the electrode at a higher electro-deposition time. As shown in Table 1, because of the well-defined peak shape and maximum developed peak current, the optimal E_{acc} and t_{acc} were chosen as 0.00 mV and 100 s, respectively.

Analytical Applications

Under the stated experimental conditions, a calibration curve was plotted using the standard additions of cyromazine in 0.1 M H_2SO_4. The obtained SWS voltammetric responses using MWCNTPE were displayed in Figure 4. A linear relationship between the peak current of cyromazine versus concentration can be established in the range of 0.41 μg/mL to 83.30 μg/mL with the analytical equation given by:

$$\mathrm{Ip}(\mu\mathrm{A}) = 2.26\ \mathrm{C}\ (\mu\mathrm{A}/\mu\mathrm{g\ mL}^{-1}) - 3.41 \quad (r = 0.999) \tag{5}$$

The limit of detection (LOD) and limit of quantification (LOQ) were obtained as 0.12 μg/mL and 0.41 μg/mL, respectively; according to the relation $k \cdot SD/b$ (where $k = 3$ for LOD and $k = 10$ for LOQ), SD is the standard deviation of the fortified blank (2.0 μg/mL), and b is the slope of the calibration curve (Currie 1999). The regression equations associated with the calibration curves (Table 2) exhibited good linearity ($r = 0.999$), that supported the validation of the proposed procedure. In addition, the comparison was made with the results provided by other type electrode, such as glassy carbon electrode (GCE) in relation with linearity, sensitivity or resistance to surface fouling. Under the same conditions, the peak current was linear to cyromazine concentration with the equation: Ip (μA) = 1.171 C (μA/μg mL^{-1}) − 0.181 ($r = 0.994$) in the range of 0.34–37.0 μg mL^{-1}(Figure 5). Limit of detection and quantification were 0.11 and 0.34 μg mL^{-1}, respectively. As comparison, the proposed method using MWCNTPE offers wider linearity range and higher sensitivity than and GCE (Table 2). On the other hand, while GCE requires polishing with slurries prepared from aluminum oxide on polishing pad before each experiment, the prepared MWCNTPE for cyromazine analysis withstands surface fouling and

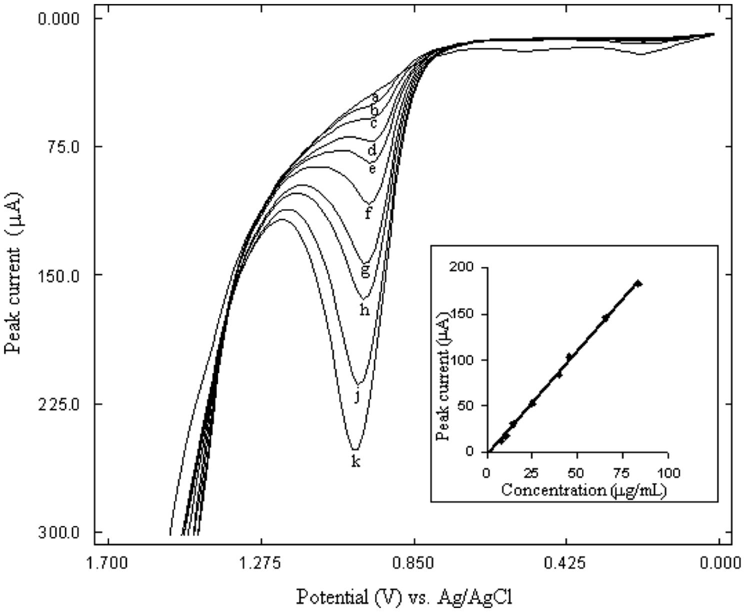


Figure 4. Square wave voltammograms and linear calibration curves (inset) obtained from standard addition of cyromazine by using MWCNTPE. a) 10.0 mL 0.1 M H_2SO_4, b) 2.50 µg/mL cyromazine, c) 5.0 µg/mL cyromazine, d) 9.80 µg/mL cyromazine, e) 14.6 µg/mL cyromazine, f) 23.8 µg/mL cyromazine, g) 37.0 µg/mL cyromazine, h) 45.4 µg/mL cyromazine, j) 65.2 µg/mL cyromazine, and k) 83.3 µg/mL cyromazine.

permits at least ten analyses after electrochemically cleaning by applying reverse potential of −1500 mV for 150 s.

The accuracy of the developed method was checked by calculating the recoveries of cyromazine from the natural water samples and agrochemical pesticide formulation Trigard®. Using the optimal conditions, calibration curves were constructed for cyromazine in river and tap water samples. The peak currents were linearly related to the pesticide concentration in river and tap water between

Table 2. Statistical parameters for the SW voltammetric determination of cyromazine

	Supporting electrolyte (0.1 M H_2SO_4)	
Parameter	MWCNTPE	GCE
Measured potential (mV)	+1110	+1050
Linearity range (µg/mL)	0.41–83.3	0.34–37.0
Slope (µA/µg mL^{-1})	2.263	1.171
Intercept (µA)	−3.41	−0.18
Correlation coefficient	0.999	0.994
LOD (µg/mL)	0.12	0.11
LOQ (µg/mL)	0.41	0.34
Repeatability of peak potential (R.S.D. %)	2.76	5.01
Repeatability of peak current (R.S.D. %)	0.76	0.39

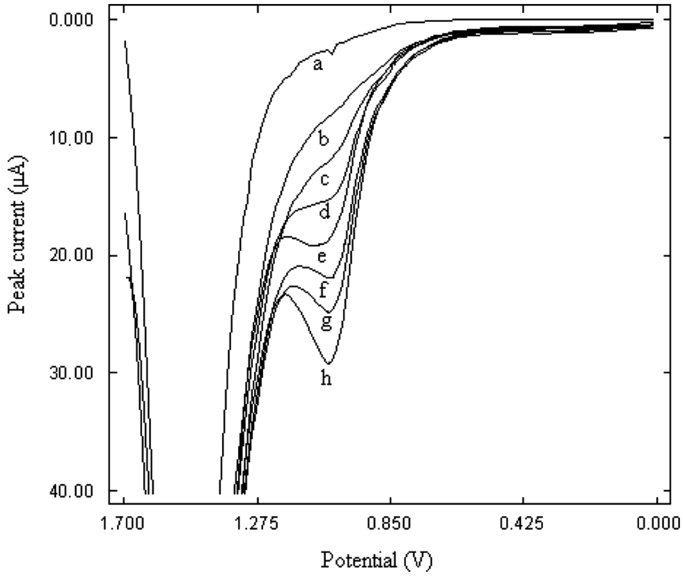


Figure 5. Square wave voltammograms obtained from standard addition of cyromazine by using glassy carbon electrode. a) 10.0 mL 0.1 M H_2SO_4, b) 5.0 μg/mL cyromazine, c) 10.0 μg/mL cyromazine, d) 19.0 μg/mL cyromazine, e) 24.0 μg/mL cyromazine, f) 28.0 μg/mL cyromazine, g) 33.0 μg/mL cyromazine, and h) 37.0 μg/mL cyromazine.

0.82–83.30 and 1.52–82.10 μg/mL. The determination was carried out by standard addition method with square wave stripping voltammetry. The results were based on the average of three replicate measurements and are summarized in Table 3.

In the case of the analysis of river water, 10.0 mL of sample obtained from Kızılırmak River, Turkey, was spiked with 50–250 μg/mL cyromazine solutions. The samples in Erlenmeyer flasks were homogenized, then they were placed in a temperature controlled water-bath and shaken for 60 min at an ambient temperature. From the supernatant, 1.0 mL of aliquots was transferred to the voltammetric cell containing 9.0 mL of 0.1 M H_2SO_4 solution. For tap water analysis, 10.0 mL of the samples were spiked using 50–250 μg/mL cyromazine solutions. After repeating the aforementioned procedure, the insecticide in spiked samples was detected by multiple standard addition using the peak appeared at +1050 mV.

Table 3. The recoveries of the cyromazine from river and tap water samples

	Recovery* (%) $\left\{\bar{X} \pm \frac{t.s}{\sqrt{n}}\right\}$	
Added (μg/mL)	River water	Tap water
0.0	N.D.	N.D.
5.0	96.7 ± 1.5	97.9 ± 2.2
10.0	101.5 ± 1.9	100.6 ± 2.3
25.0	101.0 ± 1.5	100.6 ± 3.0

*t = 95% confidence level, n = 3. N.D. not detected.

Table 4. Assay results from agrochemical pesticide formulation Trigard®

Parameters	SWSV ($n = 3$)	HPLC ($n = 3$)
Labeled claim (mass %)	75.00	75.00
Amount found (mass %)	75.36	75.51
R.S.D. (%)	0.33	0.22
Bias (%)	0.48	0.68
Student *t*-test	0.86 [2.78]*	
Variance ratio *F*-test	2.52 [19.0]*	

*The figures in parenthesis are the tabulated values of *t* and *F* at 95% confidence level.

Recoveries calculated for river and tap water samples spiked with 10 μg/mL level were 101.5 ± 1.9 and 100.6 ± 2.3 μg/mL at 95% confidence level, respectively. The sufficiently good recoveries and low relative standard deviations reflected the high accuracy and precision of the proposed square wave voltammetric method.

The optimized square wave stripping voltammetric procedure was also successfully applied to direct determination of cyromazine in agrochemical commercial formulation Trigard®. The amount of cyromazine in commercial formulation was determined by the standard addition method based on the average of three replicate measurements and the results are given in Table 4. Each measurement was repeated three times. These data gave an average cyromazine content of 75.36 ± 0.25% (by mass) for SWSV, in close agreement with the 75.0% (by mass) quoted by the manufacturer.

The cyromazine content in the Trigard® was calculated and compared statistically by student *t*-test for accuracy and variance ratio *F*-test for precision with the result obtained HPLC method (Table 4). Statistical analysis of the results by both methods using the student *t*-test and variance ratio *F*-test, show no significant difference between the performance of the two methods regarding the accuracy and precision, respectively. The experimental values of *t* and *F* at the 95% confidence level did not exceed the theoretical ones indicating the good agreement with the HPLC method. Because the proposed method offers high sensitivity, low limit of determination, easy operation, and simple instrumentation, it can be recommended for the cyromazine analysis of agrochemical pesticides.

Influences of Co-Existing Species

The performance of the voltammetric determination of cyromazine was evaluated in presence of some potential-interfering cations and anions commonly found in natural water and soil. 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 ions taken as 1, 10, and 20 times the amount of cyromazine had no serious interfering effects on the oxidation peak of cyromazine. On the other hand, effects of some other pesticides such as cyanazine, atrazine, and cymoxanil were investigated. The results for the recoveries in the presence of co-existing species are summarized in Table 5. High percentage recovery data also shows that the proposed methods are free from the interferences.

Table 5. Influence of interfering ions and pesticides on the peak current of 20 (μg/mL cyromazine

Interferent	Interferent: analyt mass ratio	Recoveries (%)	Interferent: analyt mass ratio	Recoveries (%)	Interferent: analyt mass ratio	Recoveries (%)
Zn^{2+}	1:1	100.1 ± 0.1	10:1	99.10 ± 0.1	20:1	99.30 ± 0.4
Ni^{2+}	1:1	100.3 ± 1.1	10:1	98.40 ± 2.7	20:1	101.5 ± 3.9
Mg^{2+}	1:1	100.5 ± 0.8	10:1	98.20 ± 2.5	20:1	101.4 ± 4.2
Co^{2+}	1:1	100.3 ± 0.4	10:1	103.4 ± 2.6	20:1	101.3 ± 2.9
Na^{+}	1:1	100.2 ± 0.7	10:1	99.80 ± 2.2	20:1	101.3 ± 3.2
Cl^{-}	1:1	100.5 ± 2.1	10:1	99.90 ± 1.9	20:1	98.90 ± 4.2
Cu^{2+}	1:1	102.8 ± 6.8	10:1	99.40 ± 0.8	20:1	102.0 ± 0.1
Pb^{2+}	1:1	98.1 + 2.0	10:1	97.2 + 2.5	20:1	94.0 + 1.9
Cyanazine*	1:1	99.9 ± 1.7	2:1	100.0 ± 1.1		
Atrazine*	1:1	99.8 ± 2.6	2:1	102.5 ± 1.0		
Cymoxanil*	1:1	100.2 ± 1.1	2:1	100.2 ± 2.2		

*t = 95% confidence level, n = 4 for interfering ions, n = 3 for interfering pesticides.

CONCLUSION

A novel electro-analytical method involving SWSV at MWCNTPE was proposed to determine cyromazine content in agrochemical formulation and natural water. The SWS voltammetric method presented for the quantitative determination of cyromazine 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 natural 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 be applied for the determination of cyromazine in environmental samples.

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