Ultra trace level determination of fenoxanil by highly sensitive square wave adsorptive stripping voltammetry in real samples with a renewable silver amalgam film electrode

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A B S T R A C T
A new, simple, and highly sensitive voltammetric method for the determination of low concentrations of a novel fungicide, fenoxanil (Fen), was developed using square wave voltammetry (SWV) and square wave adsorptive stripping voltammetry (SWAdSV) on a renewable silver amalgam film electrode (Hg(Ag)FE). The electrochemical reduction of Fen at the Hg(Ag)FE in Britton-Robinson (B-R) buffer at pH 6.8 was studied for the first time. The effect of the supporting electrolyte, pH, conditioning potential and conditioning time, frequency, amplitude, step potential, and accumulation potential and accumulation time were studied to select the optimum experimental conditions. The developed method can determine Fen in the concentration range of $5 \times 10^{-7}-4 \times 10^{-6}$ mol L$^{-1}$ for SWV and $1 \times 10^{-10}-9 \times 10^{-10}$ mol L$^{-1}$ for SWAdSV. Validation of the method was carried out. The method was successfully applied for trace level determination of Fen in spiked Warta River water and spiked rice samples by the standard addition method. The interference of common agents and metal ions was also examined. Fen adsorption at the mercury electrode was studied.

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1. Introduction

Nowadays, numerous types of pesticides, including insecticides, fungicides and herbicides, are regularly used in the agricultural industry. Their usage can result in long-lasting effects on the environment, and their prolonged application carries the risk of soil retention. Subsequently, these compounds may also pass into the surface and ground waters due to washing and leaching processes. For these reasons, special attention is given to the increase in health risks associated with the exposure of the human population to harmful substances occurring in the environment. Thus, the monitoring of pesticides is one of the most important tasks of modern analytical chemistry [1,2].

There are many papers dealing with the analytical determination of pesticides in agricultural and environmental samples. By far the most widely used for the detection of pesticide residues are chromatographic methods. However, as compared to those expensive optical methods, electrochemical techniques (and in particular stripping voltammetry) have many advantages in the field of practical trace analysis, such as simplicity, convenience, inexpensiveness, sensitivity, and rapidity. Thus, they are suitable for large-scale and onsite monitoring of different electrochemically active environmental pollutants [1–3].

Until recently, mercury electrodes were usually used in stripping voltammetry for the determination of trace levels of electrochemically reducible compounds or heavy metals. In the last decade, amalgam-based electrodes have been found to be suitable for many analytical applications. For example, dental amalgam electrodes have been used for the determination of heavy metals [4–6], while various solid amalgams [1,7–9] have been applied for the determination of inorganic [10] and organic [11] compounds, as well as for electrochemical analysis of nucleic acids [12], including DNA detection [13]. A relatively novel type of electrode, the silver amalgam film electrode (Hg(Ag)FE) invented by a Cracow research team, has been successfully used for the determination of several metals [14–21], some popular vitamins (C1, B1 and B2) [22], and a number of organic compounds, such as moroxidine [23], zanamivir [24], blasticidin S [25], dinotefuran [26], proguanil [27], acibenzolar-S-methyl [28], nitenpyram, thiacloprid
[29], clothianidin [29,30], thiamethoxam [31], imidacloprid [32], doxorubicin [33], and cyazofamid [34].

Fenoxanil (Fen, CAS No. 115852-48-7, Fig. 1) is a new systemic and protective fungicide with residual effects, belonging to the propionamide chemical class. Fen is melanin biosynthesis inhibitor used to control of rice blast caused by the fungus Pyricularia oryzae. It was discovered by Shell GmbH, developed jointly by BASF and Nihon Nohyaku Co. Ltd. and launched in 2000 [35].

Although Fen is a compound of biological interest, so far it has not been the subject of many chemical studies. Analytical methods for quantitative determination of Fen in rice [36–37] or in paddy plant, soil and water [38] are based mainly on gas chromatography [36–38]. Also, several multiresidue pesticide analysis methods have been developed and reported [39,40]. To the best our knowledge, no information about the electrochemical reduction properties of Fen has been described in the literature. Therefore, this paper for the first time reports an electrochemical study of Fen on a renewable silver amalgam film electrode (Hg(Ag)FE) as well as methods for its square wave voltammetric (SWV) and square wave adsorptive stripping voltammetric (SWAdSV) determination in spiked river water and rice samples.

2. Materials and methods

2.1. Instrumentation

All SWV measurements were performed using an EmStat USB potentiostat with the PSTrace software, version 2.4 (Palm Instruments BV, The Netherlands) and an M164 electrode stand (MTM Anko Instruments, Cracow, Poland). The cell stand included a three-electrode system with a renewable silver amalgam film electrode (Hg(Ag)FE, MTM Anko Instruments, Cracow, Poland) with a surface of 0.12 cm², renewed before each measurement, used as a working electrode; a silver/silver chloride electrode (Ag/AgCl, 3.00 mol L⁻¹ KCl) as a reference electrode; and a Pt wire as a counter electrode. All potentials were referred to the Ag/AgCl electrode. All measurements of pH were performed with the help of an HI 221 pH-meter (Hanna Instruments, Poland) using a combined glass membrane electrode.

Adsorption measurements were carried out in a thermostated cell at 298 K with an Autolab/GPES electrochemical analyzer, version 4.9 (Eco Chemie, Ulrecht, Netherlands). Investigations were conducted in a three-electrode cell with a hanging controlled growth mercury drop electrode (CGMDE, Entech, Cracow, Poland) as a working electrode (electrode area: 0.0095 cm², drop time: 3 s); Ag/AgCl/saturated NaCl as a reference electrode; and a platinum spiral as a counter electrode. The reference electrode was connected to the electrolytic cell via an intermediate vessel filled with the solution to be investigated.

2.2. Reagents and solutions

The analytical standard of Fen (Dr. Ehrenstorfer, Germany) was of 98.0% purity. A fresh Fen stock solution was prepared weekly at a concentration of 1 × 10⁻³ mol L⁻¹ by dissolving 3.29 mg of the pesticide in 10.0 mL of water-acetonitrile mixture (1:1, v/v) with the aid of an ultrasonic bath (5 min). All dilute solutions were prepared from the stock solution. Other pesticides (clothianidin, cyazofamid, cyanofenphos, dinofeturan, metam-sodium trihydrate, moroxydine, nitrothio-isopropyl) and metal ions (cadmium, zinc, lead, copper, nickel) were of analytical reagent grade (POCH, Gliwice, Poland; Sigma–Aldrich, Poland; Dr. Ehrenstorfer, Germany). Britton-Robinson (B-R) buffer solutions (0.04 mol L⁻¹) were used as supporting electrolytes in voltammetric measurements. The B-R buffers were prepared by successive addition of 0.20 mol L⁻¹ sodium hydroxide (POCH, Gliwice, Poland) to the mixture of 0.04 mol L⁻¹ phosphoric acid (50%, POCh, Gliwice, Poland), 0.04 mol L⁻¹ boric acid (POCH, Gliwice, Poland), and 0.04 mol L⁻¹ acetic acid (95.5%, POCh, Gliwice, Poland), to obtain the required pH value, covering the pH range of 4.5–9.5. All solutions were prepared with triply distilled water. Argon (5 N, Linde gas, Poland) in voltammetric measurements and nitrogen (99.999%, Air Products, PRM) in adsorption measurements were used without further purification. All electrochemical measurements were carried out at the ambient temperature of the laboratory (20.0–22.0 °C). All solutions were stored in a refrigerator at 4.0 °C.

2.3. Voltammetric procedures

The silver amalgam film at the Hg(Ag)FE was refreshed before each measurement [23–30]. Besides, chemical activation in 2.0% HNO₃ was applied to clean the Hg(Ag)FE surface (if needed due to the loss of sensitivity).

The general procedure used to obtain SW voltammograms was as follows: 10.00 mL of the supporting electrolyte (5.00 mL of B-R buffer mixed with 5.00 mL of water) was transferred to the voltammetric cell, and the solution was purged with pure argon for 600 s with stirring. All voltammograms were recorded under the inert atmosphere of the cell. When an initial blank was recorded, the required volumes of Fen solutions were added by means of a micropipette. If any reagents were subsequently added, the solution was purged with argon for a further 30 s. After 10 s of equilibration time, a voltammogram was recorded. The reported signals were measured without subtracting the blank solution and using the smoothing procedure available in PSTrace 2.4 software.

2.4. Adsorption measurements

The general procedure used to perform adsorption measurements was as follows: 10.00 mL of the supporting electrolyte (B-R buffer, pH 6.8) was placed in the cell and the solution was purged using high-purity nitrogen for 300 s. If any reagents were subsequently added, the solution was purged with nitrogen for further 30 s. Nitrogen was passed over the solution during the measurements.

Double layer capacity (Cₗ) was measured using the AC impedance technique with an Autolab/FRA electrochemical analyzer. The reproducibility of the average capacity measurements was ±0.5%.

For the entire polarization range, capacity dispersion was tested at different frequencies between 200 and 1000 Hz. To obtain appropriate equilibrium values of differential capacity, the linear relationship between capacity and the square root of frequency was extrapolated to zero frequency. The potential of zero charge (Eₚ) was measured for each solution by the streaming mercury electrode method with an accuracy of ±0.10 mV. Surface tension at the potential of zero charge (γₛ) was measured using the method of the highest pressure inside the mercury drop presented by Schiffrin. Surface tension was determined with an accuracy of ±0.2 mN m⁻¹. The details are described in the literature [41,42].
2.5. Determination of Fen in real samples

2.5.1. Spiked river water samples

River water samples for analysis were collected from the Warta River (Pławni, Poland) and stored in a refrigerator at 4.0 °C. The samples were spiked with the analyte without any previous treatment or filtration except dilution, and analyzed within one week of collection.

**SWV procedure:** The preparation of spiked river water samples was conducted as follows: 100.0 μL of the Fen stock solution was transferred to a 50.0 mL calibrated flask and filled to the mark with river water.

**SWAdSV procedure:** The preparation of spiked river water samples was as follows: 100.0 μL of Fen was diluted in a 100.0 mL calibrated flask and filled to the mark with river water. Next, 50.00 mL of this diluted Fen solution was transferred again to a 50.0 mL calibrated flask and filled to the mark with river water.

First, 5.00 mL of B-R buffer, pH 6.8 and 5.00 mL of river water were placed in the voltammetric cell, and SWV and SWAdSV curves of the blank were recorded. Next, 5.0 mL of B-R buffer, pH 6.8 and 5.00 mL of spiked river water were placed in the voltammetric cell. When SW and SWAdSV voltammograms of spiked river water samples were recorded, the standard addition method was applied. Consecutive additions of Fen were made with a micropipette to the voltammetric cell (the concentrations were: 1 × 10⁻⁶ mol L⁻¹ and 2 × 10⁻⁶ mol L⁻¹ for SWV; 2 × 10⁻¹⁰ mol L⁻¹ and 4 × 10⁻¹⁰ mol L⁻¹ for SWAdSV). Voltammograms were recorded after each addition, and Fen recovery was calculated after five replicate experiments.

2.5.2. Rice samples

2.5.2.1. Preparation of untreated rice samples. For this experiment, white long-grain rice was obtained from a local supermarket. A rice sample (30 g) was crushed in a mortar into small particles. To the sample, 100.0 mL of acetone was added, the mixture was carefully shaken manually, filtered using a Büchner funnel, and the organic phases were collected. The solid phase was washed twice with 20.0 mL of acetone, and the organic extract was left to dry at 25.0 °C. The residue was dissolved in 5.00 mL of 0.1 mol L⁻¹ HCl. Next, the acidic solution was transferred to a 50.0 mL flask and filled up to the mark with acetone.

Next, 5.00 mL of this solution was transferred to the voltammetric cell with 5.00 mL of B-R buffer, pH 6.8. After SWV and SWAdSV curves of the spiked rice sample were recorded, the standard addition method was applied. Consecutive additions of Fen were made with a micropipette to the voltammetric cell (the concentrations were: 1 × 10⁻⁶ mol L⁻¹ and 2 × 10⁻⁶ mol L⁻¹ for SWV; 2 × 10⁻¹⁰ mol L⁻¹ and 4 × 10⁻¹⁰ mol L⁻¹ for SWAdSV). Voltammograms were recorded after each addition, and Fen recovery was calculated in five runs.

3. Results and discussion

3.1. The influence of pH and SW parameters

In order to achieve optimum experimental conditions for the determination of Fen using Hg(Ag)FE, extensive studies were performed. The voltammetric behavior of Fen at the Hg(Ag)FE depends on several factors, such as pH and SW parameters. In a preliminary study, the electrochemical behavior of Fen over a pH range from 4.5 to 9.5 was investigated (Fig. 2). Britton-Robinson (B-R) buffers were chosen as supporting electrolytes. First, the peak height increased with increasing pH (from 4.5 to 6.8), and next the signal decreased (inset of Fig. 2), indicating the involvement of protons in the reaction mechanism. The most symmetrical and the highest reduction signal of Fen at a potential of about −1.35 V (3 × 10⁻⁵ mol L⁻¹) was achieved in B-R buffer at pH 6.8. The Hg(Ag)FE, being a solid working electrode, requires renewal and conditioning of the sensor surface. It was found that conditioning potential \(E_{\text{cond}}\) can influence the peak current and peak potential [30]. Therefore, the effect of conditioning potential on the SWV signals of the fungicide was the next critical choice. The influence of \(E_{\text{cond}}\) on the behavior of Fen (3 × 10⁻⁵ mol L⁻¹) was studied at a conditioning time \(t_{\text{cond}}\) of 10 s in the potential range from 0 V to −2.00 V. It was found that in this case conditioning potential did not significantly influence the reduction peak current (B-R buffer, pH 6.8). Therefore, \(E_{\text{cond}} = −1.20\) V was chosen as the optimum conditioning potential for further measurements. Next, the impact of the conditioning time \(t_{\text{cond}}\) of Fen was investigated in the range from 0 s to 100 s. It was found that \(t_{\text{cond}}\) had a strong effect on the Fen peak current and peak potential. The maximum peak height of Fen was achieved for \(t_{\text{cond}} = 20\) s. A conditioning time

![Fig. 2. Effect of pH on the SWV signal of 3 × 10⁻⁵ mol L⁻¹ Fen at Hg(Ag)FE recorded in B-R buffer: pH (1) 4.5, (2) 5.7, (3) 6.8, (4) 7.7, and (5) 8.6. The insets shows the dependence of the SWV peak current on pH. Measurement parameters: \(E_{\text{cond}} = −1.70\) V, \(t_{\text{cond}} = 10\) s, \(f = 50\) Hz, \(E_m = 50\) mV, \(ΔE = 5\) mV, and \(t_{eq} = 10\) s.](image-url)
The presence of a nitrile group in the structure of Fen (Fig. 1) gives rise to a voltammetric reduction peak at about $-1.35 \text{ V}$ at $E_{\text{SW}}$.

### Table 1

The zero charge potential ($E_z$) (CGMDE) vs. Ag/AgCl/saturated NaCl electrode and the surface tension at the zero charge potential ($\gamma_z$) of the double layer interface Hg/B-R buffer and Hg/B-R buffer in the presence of different concentrations of Fen.

<table>
<thead>
<tr>
<th>$C_{\text{Fen}}$ [mol L$^{-1}$]</th>
<th>$E_z$ [mV]</th>
<th>$\gamma_z$ [mN m$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>406.7</td>
<td>424.7</td>
</tr>
<tr>
<td>3.0</td>
<td>405.2</td>
<td>423.8</td>
</tr>
<tr>
<td>6.0</td>
<td>403.7</td>
<td>423.0</td>
</tr>
<tr>
<td>9.0</td>
<td>403.0</td>
<td>420.5</td>
</tr>
<tr>
<td>12.0</td>
<td>402.3</td>
<td>417.9</td>
</tr>
<tr>
<td>15.0</td>
<td>401.2</td>
<td>416.3</td>
</tr>
<tr>
<td>20.0</td>
<td>395.0</td>
<td>415.4</td>
</tr>
<tr>
<td>25.0</td>
<td>395.0</td>
<td>414.6</td>
</tr>
<tr>
<td>30.0</td>
<td>394.0</td>
<td>409.5</td>
</tr>
</tbody>
</table>

3.2. Electrochemical behavior of Fen

The influence of the parameters of potential modulation, such as: frequency ($f$), amplitude ($E_{\text{SW}}$), and step potential ($\Delta E$) [43–45], were also studied because of their influence on the voltammetric signal of Fen at about $-1.35 \text{ V}$.

The effect of $E_{\text{SW}}$ was investigated in the range from 10 mV to 200 mV. At amplitudes in the range of 10–70 mV, the peak current increased linearly with increasing $E_{\text{SW}}$. Amplitudes higher than 70 mV caused a non-linear growth of the peak (plateau) and a distortion of the voltammograms. In further work, $E_{\text{SW}} = 60 \text{ mV}$ was applied. The influence of frequency (5–100 Hz) on the peak current was also studied. In the investigated range, peak intensities increased with increasing $f$. However, frequencies higher than 50 Hz caused a distortion of peak shape. The best-shaped signal was obtained for $f = 50 \text{ Hz}$, and this value was chosen as the optimum in subsequent studies. The influence of step potential ($\Delta E$) was studied in the range from 1 mV to 10 mV. The peak current increased linearly from 1 mV to 6 mV and was well-shaped. Step potential levels higher than 6 mV caused a distortion of peak shape. The best results were obtained for 2 mV, and this value was used in further analytical studies. Equilibration time ($t_{\text{eq}}$), whose value was changed in the range from 0 s to 50 s, did not significantly influence the peak current. Consequently, $t_{\text{eq}} = 10 \text{ s}$ was chosen as the optimum equilibrium time for further analytical measurements.

To improve the sensitivity and the detection limit of the method, the influence of accumulation potential ($E_{\text{acc}}$) and accumulation time ($t_{\text{acc}}$) were also studied. The relationship between the SWAdSV peak current and $E_{\text{acc}}$ was studied at $t_{\text{acc}} = 10 \text{ s}$, in the potential range from 0 V to $-1.20 \text{ V}$ for a Fen concentration of $5 \times 10^{-6} \text{ mol L}^{-1}$. It was found that in this case accumulation potential did not significantly influence the peak current of Fen. $E_{\text{acc}} = -0.60 \text{ V}$ was used as the optimum accumulation potential for further analytical studies. Next, the effect of accumulation time on the peak current was investigated in the range from 0 s to 100 s at a Fen concentration level of $5 \times 10^{-6} \text{ mol L}^{-1}$. It was found that the observed Fen response was highly sensitive to deposition time. The maximum response was achieved with $t_{\text{acc}} = 60 \text{ s}$, and this value was used in all subsequent measurements. It should be noted that a further increase in accumulation time caused a significant decrease in the voltammetric response of Fen. Such behavior suggests a high affinity of molecules to the electrode surface [30,46].

![Diagram](image-url)
the Hg(Ag)FE. Literature data describe the electrochemical reduction of such compounds at different types of working electrodes in acidic, neutral, and alkaline solutions [47–49]. It has been shown that both pH and electrode material play an important role in the electrochemical behavior of nitriles [47]. Until recently, nitriles were considered to be electrochemically non-reducible in aqueous solutions at mercury electrodes [49], but reducible at nickel, copper, and silver electrodes [50]. However, some papers have reported nitrile reduction at mercury electrodes [47]. It has been found that in acidic aqueous media aromatic nitriles undergo an irreversible four-electron reduction with the formation of the corresponding amine [49]. Under neutral conditions, aromatic nitriles undergo a two-electron reduction with the formation of a cyanide ion, which may be an irreversible process [47]. Fenoxanil does not have this kind of conjugated bonds, so based on the literature [49], it seems that in the present case (in almost neutral conditions) Fen is reduced to an imine (Scheme 1, B) and then hydrolyzed (through the EC mechanism) to an aldehyde or another product (Scheme 1, C).

The technique of cyclic voltammetry (CV) reveals the basic characteristics of the studied signals regarding the mechanism of electrode reactions, their kinetic parameters, and reversibility of the system in a relatively short time. To explain the nature of the electrode process, the CV behavior of Fen was investigated in the potential range from −0.10 V to −1.60 V at a concentration level of 1 × 10⁻⁴ mol L⁻¹ in B-R buffer at pH 6.8. Therefore, the potential scan rate (v) was changed from 0.025 V s⁻¹ to 0.400 V s⁻¹ during the experiment.

A typical cyclic voltammogram (inset in Fig. 3) shows one peak in the cathodic run (Epc between −1.41 V and −1.44 V) and one anodic peak during the reverse scan (Epa between −1.35 V and −1.39 V, depending on the scan rate). The obtained results suggest an electrochemically quasi-reversible system, which is consistent with the proposed pathway of Fen reduction. In practice, the following diagnostic criteria are used to characterize the cyclic voltammogram of a reversible process: (1) Peak potential separation is \( \Delta E_{pv} = E_{pca} - E_{pca} = 59/n \) mV at all scan rates at 25 °C; (2) The peak current ratio is \( I_{pc}/I_{pa} = 1 \) at all scan rates; and (3) Peak current (Ip) as a function of the square root of the scan rate (\( v^{1/2} \)) is independent of the scan rate. Based on these criteria of reversibility, the following observations have been made: (1) Peak potential separation (\( \Delta E_{pv} \)) decreases with increasing scan rate. Additionally, in the presented case \( \Delta E_{pv} \) is between 39 and 84 mV, which would suggest an electrochemically quasi-reversible system. (2) The \( I_{pc}/I_{pa} \) ratio differs from 1 (it is in the range of 3.3–5.3, with \( I_{pc} \) being about 4 times higher than \( I_{pa} \)). These results seem to indicate that the reduced form of the analyte, which can be oxidized, is non-renewable, which means that the reduced form may undergo an EC mechanism. (3) The relationship between the peak current (Ip) and the square root of the potential scan rate (\( v^{1/2} \)) is non-linear (Fig. 3). These results suggest that the process is quasi-reversible.

The cathodic (Ip) and anodic (Ipa) peak currents are directly proportional to the scan rates (v). Moreover, a non-linear increase in the reduction and oxidation peak currents (Ip and Ipa) with the square root of the scan rates (\( v^{1/2} \)) was observed. This clearly proves that both cathodic and anodic currents are controlled by the adsorption of the electroactive species at the electrode surface. To confirm the above results, the relationship between the logarithm of the peak current (\( \log I_{pc} \)) and the logarithm of the scan rate (\( \log v \)) was analyzed. The values of k in the equation \( I_{pc} = Av^k \) were expected to be 1 for adsorption-controlled and 0.5 for diffusion-controlled systems [51,52]. Regression of the relationship between \( \log I_{pc} \) and \( \log v \) gave slopes equal to 1.031 (for the cathodic peak) and 1.064 (for the anodic peak) with correlation coefficients of the straight line \( R^2 = 0.993 \) and \( R^2 = 0.990 \), respectively, indicating that the discussed processes are of adsorptive nature.

3.3. Adsorption studies

Fig. 4 presents differential capacity curves of the double layer interface Hg/B-R buffer (pH 6.8) and Hg/B-R buffer (pH 6.8) + Fen.

Analysis of differential capacity curves (Fig. 4) showed that a characteristic maximum (\( E_{p} = -600 \) mV) occurs on the curve obtained for the supporting electrolyte (B-R buffer, pH 6.8) without Fen, which can be related to a change in the orientation of water molecules in the double layer. The presence of Fen in the support-

![Fig. 4](image)

**Table 2**

Regression data of the calibration graphs for the quantitative determination of Fen at Hg(Ag)FE, B-R buffer, pH 6.8 by SWV and SWAdSV using Hg(Ag)FE.

<table>
<thead>
<tr>
<th></th>
<th>SWV</th>
<th>SWAdSV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration range</td>
<td>Concentration range</td>
</tr>
<tr>
<td>(mol L⁻¹)</td>
<td>5.0 × 10⁻⁶ – 1.0 × 10⁻⁴</td>
<td>1.0 × 10⁻¹⁰ – 1.0 × 10⁻⁸</td>
</tr>
<tr>
<td>Slope (A L mol⁻¹⁻¹)</td>
<td>4.0 × 10⁻⁶</td>
<td>9.0 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Intercept (A)</td>
<td>-0.40 × 10⁻⁷</td>
<td>-1.3 × 10⁻⁶</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>Number of measurements</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>LOD (mol L⁻¹)</td>
<td>6.5 × 10⁻⁸</td>
<td>2.8 × 10⁻¹⁰</td>
</tr>
<tr>
<td>LOQ (mol L⁻¹)</td>
<td>2.2 × 10⁻⁷</td>
<td>9.4 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

\( a \) LOD = kSD/b (k = 3 for LOD).  
\( b \) LOQ = kSD/b (k = 10 for LOQ).
ing electrolyte solution (B-R buffer, pH 6.8) caused a significant decrease of differential capacity in the studied potential range (from \(-400\) mV to \(-1200\) mV). It should be emphasized that adsorption peaks of Fen in the investigated potential range on the differential capacity curves were not observed, while at \(E_p = -1350\) mV and at Fen concentrations higher than \(1.2 \times 10^{-5}\) mol L\(^{-1}\) a desorption peak seemed to be observed. The height of the desorption peak increased with increasing adsorbate concentration in the supporting electrolyte solution.

The values of zero charge potential \(E_z\) and surface tension at the zero charge potential \(\gamma_{SL}\) of the double layer interface Hg/B-R buffer and Hg/B-R buffer in the presence of different concentrations of Fen are presented in Table 1. The values of \(E_z\) measured for Fen were shifted to less negative potentials with increasing Fen concentration. These results suggest that the positive end of the Fen molecule (in this case, the carbon in the nitrile group) is strongly adsorbed on the mercury electrode surface and causes a non-planar surface organization of the molecule [53]. It is also worth noting that an increase in Fen concentration in the supporting electrolyte (B-R buffer, pH 6.8) results in increased adsorption of the molecule on the mercury electrode surface. This conclusion is confirmed by a decreased surface tension at the zero charge potential \(\gamma_{SL}\) caused by Fen [41].

3.4. Analytical characteristic of Fen

Quantitative measurements of Fen at the Hg(Ag)FE were performed using SWV and SWAdSV. The analytical performance was studied under the optimum conditions described in Section 3.1. The applicability of the SWV and SWAdSV methods for the determination of Fen was tested as a function of peak current intensity \(I_p\) and increasing Fen concentration \(c_{Fen}\). The linear ranges were from \(5 \times 10^{-7}\) mol L\(^{-1}\) to \(4 \times 10^{-6}\) mol L\(^{-1}\) for SWV (Fig. 5a) and from \(1 \times 10^{-10}\) mol L\(^{-1}\) to \(9 \times 10^{-10}\) mol L\(^{-1}\) for SWAdSV (Fig. 5b). The characteristics of the corresponding calibration curves are shown in Table 2.

The limits of detection (LOD) and quantification (LOQ) were calculated for Fen from the calibration curves as follows: LOD = \(3SD/b\) and LOQ = \(10SD/b\). Standard deviations (SD) were calculated for the intercept (five runs), and \(b\) stands for the slope of the calibration graphs [54]. The repeatability (one day) of the voltammetric procedure was estimated with five replicates at each of the studied Fen concentrations. In order to check the correctness of the method, its precision and the recovery of the method were also calculated for different concentrations in the linear ranges. The results are presented in Table 3.

3.5. Analytical applications

3.5.1. Analysis of spiked river water

The optimized voltammetric procedure was successfully applied for the determination of Fen in the spiked samples of Warta River water, prepared as described in Section 2.5.1. As can be seen from the voltammograms (Fig. 6, curve (0)), no interferences were observed from the river water components. The applicability of the developed SWV and SWAdSV procedures (five replicates) was tested with the standard addition method. The recovery results for Fen in spiked river water are given in Table 4. The method was found acceptable for the determination of Fen in spiked Warta River water.

3.5.2. Analysis of untreated rice samples

The untreated rice solution was studied under the optimized voltammetric parameters to check for interferences derived from rice. The calibration curves obtained in this medium (as described in Section 2.5.2.1) for Fen show a linear relationship between the peak current and concentration in the range from \(5 \times 10^{-7}\) mol L\(^{-1}\) to \(3 \times 10^{-6}\) mol L\(^{-1}\) for SWV and from \(1 \times 10^{-10}\) mol L\(^{-1}\) to

<table>
<thead>
<tr>
<th>SWV</th>
<th>Added [10(^{-6}) mol L(^{-1})]</th>
<th>Found(^a) [10(^{-6}) mol L(^{-1})]</th>
<th>Precision RSD</th>
<th>Recovery(^b) [%]</th>
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<td>0.53 ± 0.09</td>
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<td>106.6</td>
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<td>1.06 ± 0.10</td>
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<td>105.7</td>
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<th>SWAdSV</th>
<th>Added [10(^{-10}) mol L(^{-1})]</th>
<th>Found(^a) [10(^{-10}) mol L(^{-1})]</th>
<th>Precision RSD</th>
<th>Recovery(^b) [%]</th>
</tr>
</thead>
<tbody>
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</table>

\(^a\) t(S/n\(^{1/2}\)), \(p = 95\%\), \(n = 5\).
\(^b\) Recovery = 100 \% + |(Found–Added)/Added| \times 100\%.

Fig. 6. (a) SWV and (b) SWAdSV curves of Fen determination in the spiked river water samples at Hg(Ag)FE using the standard addition method; (a) (0) blank, (1) spiked river water sample, (2) as (1) + 1.0 \times 10^{-6} mol L\(^{-1}\), and (3) as (2) + 1.0 \times 10^{-6} mol L\(^{-1}\); (b) (0) blank, (1) spiked river water sample, (2) as (1) + 0.2 \times 10^{-10} mol L\(^{-1}\), and (3) as (2) + 0.2 \times 10^{-10} mol L\(^{-1}\). The conditions were the same as in Fig. 5.
five replicates were performed as described in Section 2.5.2.2. The results of the recovery and precision results for Fen are given in Table 4. The methods are sufficiently accurate and precise for the determination of Fen in rice samples.

### 3.6. Effect of interferences

Finally, we checked whether the commonly used pesticides, such as: clothianidin, cyanoephos, cyazoafamid, dinotefuran, moroxydine, metam-sodium trihydrate, and nitrothal-isopropyl, and also heavy metal ions such as: cadmium, zinc, lead, and copper, would interfere with Fen determination by the developed method under the optimized experimental conditions. The concentration of Fen in the voltammetric cell was equal to $1 \times 10^{-6}$ mol L$^{-1}$ and was fixed during the study, whereas the other pesticides and ions were present at levels ranging from $1 \times 10^{-6}$ mol L$^{-1}$ to $1 \times 10^{-4}$ mol L$^{-1}$. The corresponding ratios of the interferents to Fen concentration were: 0.01, 0.1, 0.5, 1, 10, 50, and 100. The presence of cyazoafamid, metam-sodium trihydrate, and moroxydine exhibited a minor effect on the recorded peak current. Dinotefuran and clothianidin caused a pronounced increase and distortion of the measuring signal only at concentration ratios of 50 and 100. On the other hand, the presence of cyanophenpos and nitrothal-isopropyl almost always hindered the peak related to the presence of Fen in the solution (only concentration ratios of 0.01, 0.1, and 0.5 did not increase the signal). The presence of common heavy metal ions generally had no significant effect on the measured peak current of Fen. Copper and lead ions caused a minor increase in the recorded Fen signal, while the presence of zinc and cadmium caused a pronounced increase in the measured peak current only at concentration ratios of 50 and 100.

### 4. Conclusions

The electrochemical behavior of Fen at the Hg(Ag)FE was studied for the first time. New square wave voltammetric and square wave adsorptive stripping voltammetric methods for the determination of Fen were developed, under optimized experimental conditions. Cyclic voltammetric experiments showed that the electrode mechanism is a quasi-reversible reduction controlled by the adsorption of Fen. The results of adsorption measurements indicate that the molecules are adsorbed with the positive end of Fen molecules pointing to the mercury surface and suggest that the molecules are not placed flat on the surface. An analytical method for Fen determination was developed. The behavior of Fen at the Hg(Ag)FE provides a useful tool for the detection and quantification of Fen at trace concentration levels in selected samples, such as river water and rice. The effect of other commonly used pesticides, including clothianidin, cyanoephos, cyazoafamid, dinotefuran, moroxydine, metam-sodium trihydrate, and nitrothal-isopropyl, as well as heavy metal ions, including cadmium, zinc, lead, and copper, was also studied.

### Conflict of interest

There is no conflict of interest.

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### References
