Electrochemical behavior and determination of bromethrin pesticide residues in soil, water and agricultural formulations

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Abstract

An electroanalytical method has been developed for the determination of bromethrin pesticide by differential pulse adsorptive stripping voltammetry on a hanging mercury drop electrode in universal buffer as supporting electrolyte. The best adsorption conditions were found to the reduction of >C=*=C< at pH 6.0, an accumulation potential of -1.2V and an accumulation time of 60 Sec. The effect of stirring rate, scan rate, pulse amplitude and purge time were examined for the optimization of instrumental conditions and observed linearity range at hanging mercury drop electrode (HMDE) has been found to be 2.14×10^-8 mol.L^-1 to 2.13×10^-4 mol.L^-1 with a lower detection limit 2.06×10^-9 mol.L^-1. The average recoveries obtained for bromethrin in soil and water samples ranged from 95.33 to 98.40% with RSD of 2.01% . The method has been satisfactorily applied to the determination of bromethrin in soil and water samples of Srikalahasti and chandragiri agricultural regions.

Key Words: bromethrin, soil and water samples, agricultural formulations, HMDE and voltammetry.

Introduction

Synthetic pyrethroid insecticides are widely used because they are effective against many insects, pests and show favourable selective toxicity towards insects and low toxicity to mammals and birds. Their main use include field-treatments in houses and stable premises and on animals to control ecto- and endo- parasites. The effect of synthetic pyrethroid on various non-target organisms have been reviewed by David and Somasundaram2 Huston and Cassida,3,4 reported that synthetic pyrethroids are detoxified quickly in mammals as they encounter powerful esterases and monooxygenates before reaching sensitive nerve centres. The residue analysis of pyrethroids has been reviewed by Miyamoto5, Papadopoulouandour Kidou6,7 and Sharp.8

Bromethrin (5-benzyl-3-furymethyl (1RS,3RS;1RS,3SR)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropanecarboxylate) is registered as selective insecticide, which act by killing insects and commonly used as controlling for food grain pest. The purpose of the present investigation was to elucidate the electrochemical reduction mechanism and electrode kinetics by employing advanced electrochemical techniques and to develop analytical procedures for the quantitative estimation of bromethrin in soil, water and agricultural formulations.

Numbers of analytical techniques mostly chromatographic methods9-12 are reported in the literature for the determination of synthetic pyrethroids. Miyamoto13 explained Degradation, Metabolism and Toxicity of Synthetic Pyrethroids, Synthetic pyrethroidal compounds were undergo biodegradation in mammals both oxidatively and hydrolytically, and depending on the type of compound, either of the pathways may predominate. Electrochemical studies of some synthetic pyrethroid insecticides have been carried out.14-19 Voltametric behaviour of synthetic pyrethroid insecticides and their determination in environmental and agricultural samples have been reported.20-28

In the present work the emphasis has been on electrochemical study of bromethrin pesticide to get more information on the reduction mechanism of the compound and the electrode kinetics concerned, employing advanced electrochemical techniques. It is chosen to get more
information on the electrode kinetics as well as reduction mechanism of >C=C group by employing advanced electrochemical techniques such as cyclic voltammetry, adsorptive stripping voltammetry. Therefore, a rapid and sensitive Adsorptive stripping voltammetry method has been applied to determine the bromethrin pesticide in soil and water samples.

Experimental

Apparatus and Reagents

Polarographic analyser model ELICO CL-362 supplied from an Elico Ltd, Hyderabad with EPSON LX-300+ recorder was used for polarographic measurements. A three-electrode system consisting of a medium size hanging mercury drop electrode (HMDE), a Pt wire as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode was used. All reported potentials were referenced to the SCE electrode. Solutions were deoxygenated with high purity nitrogen for 10–15 min prior to each experiment. An Elico LI-120 digital pH meter supplied by Hanna instruments (Italy) was used to measure the pH of the buffer solutions.

Universal buffers of pH range 2.0 to 12.0 are used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M citric acid and 0.1M trisodium orthophosphate (Sigma-Aldrich, supplied by SD Fine Chemicals, India). The purity of the pesticide samples which obtained from Rankem fine chemicals limited, Bangalore, tested by thin layer chromatography and also melting point determinations. Stock solution (2.13×10⁻⁶ mol L⁻¹) was prepared by dissolving bromethrin in methanol (Sigma-Aldrich, supplied by SD Fine Chemicals, India). All dilute solutions were freshly prepared daily from the stock solution. Reagents were used for the overall process are Analytical grade.

General Procedure

10 mL (1 mL known concentrated bromethrin solution and 9 mL of buffer solution) of electro active solution was transferred into a 100 mL of measuring flask, to this 50 mL of 1M KCl solution and 2.5 mL of 0.2% gelatin solution were added. This was diluted up to the mark. From this 10 mL of the solution was transferred in to voltammetric cell and then deoxygenated with nitrogen gas for 10 min. After the voltammogram was recorded, the process was repeated for different concentration solutions at various pH values under similar conditions. To the overall experiment optimum temperature was chosen as 25°C.

Result and discussion

The electrochemical behavior of bromethrin was examined over the pH range 2.0-12.0 by typical voltammograms of differential pulse adsorptive stripping voltammetry and cyclic voltammetry. Fig.1 shows differential pulse adsorptive stripping voltammograms for 1.0×10⁻⁵ mol L⁻¹ bromethrin at HMDE. The DP-AdSV peak obtained for the reduction of >C=C< group in bromethrin at pH 6.0.

![Fig.1](image1.png)

**Fig.1.** Typical differential pulse adsorptive stripping voltammogram of bromethrin at HDME; of (1) blank solution, concentration: 2.13×10⁻⁶ mol L⁻¹ (2) pH of 2.0 (3) pH of 4.0 (4) pH of 6.0; Drop time: 2 sec; accumulation potential: -1.2 V; accumulation time: 60 sec; scan rate: 40 mVs⁻¹; pulse amplitude: 50 mV.

![Fig.2](image2.png)

**Fig.2.** Effect of pH on bromethrin at HDME; concentration: 2.13×10⁻⁶ mol L⁻¹; drop time: 2 sec; accumulation potential: -1.2 V; accumulation time: 60 sec; scan rate: 40 mVs⁻¹; pulse amplitude: 50 mV.

![Fig.3](image3.png)

**Fig.3.** Effect of accumulation potential on the DP-AdSV response of bromethrin at HDME; pH = 6.0 concentration: 2.13×10⁻⁶ molL⁻¹; drop time: 2sec; accumulation time: 60sec; scan rate: 40mVs⁻¹; pulse amplitude: 50 mV.
Effect of Scan Rate
HMDE. studies an accumulation time of 60 sec. was chosen at curre
accumulation time (Fig.4) was studied at concentration of 2.13×10^{-6}
molL^{-1}; drop time: 2 sec; accumulation potential: -1.2 V; scan rate: 40 mVs^{-1}; pulse amplitude: 50 mV.

Effect of pH
The influence of the pulse amplitude was
investigated by recording a maximum developed and sharper DP-AdSV peak for 2.13×10^{-6} molL^{-1} bromethrin at t_{acc}: 60 sec, E_{acc}: -1.2 V, scan rate: 40 mVs^{-1} and pulse amplitude : 50 mV, optimum temperature: 25°C.

Cyclic Voltammetric study
The effect of pH on the voltammograms is investigated by recording the current voltage curves for non-aqueous solutions of bromethrin at a concentration of 2.13×10^{-6} mol L^{-1} in universal buffer system over the pH range of 2.0 to 12.0. bromethrin exhibits a single, well-defined two-electron reduction peak in cyclic voltammogram which is attributed to the reduction of >C=C< group to the corresponding saturated product at pH 6 (Fig. 5). The peak current (ip) is dependent on scan rate (v) and pH of the supporting electrolyte. The peak potentials are found to be varied towards the more negative side with increase in pH 6.0. The determination of number of electrons (n) involved during the electrode process, in bromethrin, has been carried out by millicoulometry. According to this technique, ‘n’ is found to be two for bromethrin in acidic as well as neutral and basic media. In the present investigation, controlled potential electrolysis is employed to get the reduction product. Controlled potential electrolysis has been carried

Fig.4. Effect of accumulation time on the DP-AdSV response of bromethrin at HDME; pH = 6.0 concentration: 2.13×10^{-6} molL^{-1}; drop time: 2 sec; accumulation potential: -1.2 V; scan rate: 40 mVs^{-1}; pulse amplitude: 50 mV.

Fig.5. Typical cyclic voltammogram of bromethrin at pH 6.0; concentration: 2.13×10^{-6} molL^{-1}; drop time: 2 sec; accumulation potential: -1.2 V; accumulation time: 60 sec; scan rate: 40 mVs^{-1}; pulse amplitude: 50 mV.
Table 1. Recoveries of bromethrin in soil and water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount added in mM</th>
<th>Found mM</th>
<th>*Recovery (%)</th>
<th>Standard deviation</th>
<th>Relative Standard deviation (%)</th>
</tr>
</thead>
<tbody>
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<td>Soil sample</td>
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<tr>
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<td>4.87</td>
<td>97.40</td>
<td>0.091</td>
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<td>0.176</td>
<td>1.79</td>
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<td>97.60</td>
<td>0.254</td>
<td>1.72</td>
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<tr>
<td>Water sample</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>60.0</td>
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<td>0.990</td>
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*each value is the average of 3 determinations.

Table 2. Recoveries of bromethrin in rice and corn samples

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<th>Sample</th>
<th>Amount added in mM</th>
<th>Found mM</th>
<th>*Recovery (%)</th>
<th>Standard deviation</th>
<th>Relative Standard deviation (%)</th>
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<td>96.00</td>
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<tr>
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<td>0.848</td>
<td>1.15</td>
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</tr>
</tbody>
</table>

*each value is the average of 3 determinations.

Scheme 1. Reduction mechanism of bromethrin

Electrolysis of the electroactive substance has been carried out in a modified cell with a three-electrode system. Electrolysis was conducted at −1.2 V vs SCE, and the product formed after the controlled potential electrolysis is identified and confirmed as the saturated product of the corresponding electroactive species by IR spectral data as absence of C=C stretch at 1,640–1,680 cm⁻¹, C–H stretch 2,960 cm⁻¹, C–H bend 1,465 cm⁻¹.

**Kinetic Data**

Kinetic parameters such as diffusion coefficient,
transfer coefficient and heterogeneous forward rate constant values are evaluated and reported in Table 1. The diffusion coefficient values are noticed to be in good agreement in all the techniques. This indicates the electrode process to be diffusion controlled and adsorption on to the electrode surface without any kinetic complications.

The heterogeneous forward rate constant values are found to decrease with increase in pH of the supporting electrolyte which may account for the shift of reduction potentials towards more negative values with increase in pH. This trend is particularly evident where the proton transfer is involved in the electrode process. Possibly an increase in pH decreases the dissociation constant of the protonated species and these factors affect the protonation rate and consequently the reduction potentials are shifted to more negative potentials. Based on the results obtained from all the techniques, the electrochemical reduction mechanism of bromethrin is as shown in scheme.1.

**Effect of Interferences**

The proposed method was free from interferences in bromethrin and also other constituents present in soil, water, rice and corn samples. The proposed method was free from interferences in phenothrin and also other constituents present in vegetables and storage bags of wheat and rice. We examined other commonly used pesticides like bromethrin, bifenthrin, and dimethrin. In the presence of these compounds (at pH 6.0, −0.6 V), the presence of the above pesticides causes no significant changes in the peak potential of the voltammetric reduction peaks obtained for bromethrin, since bifenthrin gives a reduction peak at −1.35V and shifted to more negative potentials than those of bromethrin. Therefore, the proposed method does not involve the elaborate cleanup procedures with the other methods.

**Application**

Soil, water, and Rice sample were collected from Gajula Pelluru Vill, B.N.Kandriga Mandal, Chittoor Dist of Andhra Pradesh, India. Corn sample were collected from Arala Vill, Chandragiri Mandal, Chittoor Dist of Andhra Pradesh, India. Aliquots (50 g) of water and soil, were added separately with known amounts of bromethrin and kept constant for 24 hours. After this period, the mixture was extracted with 20ml of methanol three times. The solvent evaporated to around 1 mL and was dissolved in methanol and subjected to voltammetry separately. By means of standard addition method the quantity of pesticide was estimated. The same method is applied to the agricultural samples i.e. rice and corn. The average recoveries obtained for bromethrin in water, soil, rice and corn samples ranged from 95.33 to 98.40 % and results are given in Table 3 and 4.

**Conclusions**

The electrochemical study of bromethrin was successfully studied by adsorptive stripping voltammetry. Strongly adsorbed on the surface and the transference of 2 electrons per bromethrin molecule. In the analytical application, adsorptive stripping voltammetry showed to be a very fast and sensitive technique that allows reaching detection limits in the range of trace analysis in natural soil water and agricultural samples applied to the agricultural sample formulations. This is one major advantages of this electroanalytical technique since it is rapid and versatile technique with very less expensive.

**References**

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