Differential pulse anodic stripping voltammetric determination of endosulfan

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Received 19 September 1997; revised 15 July 1998

A differential pulse anodic stripping voltammetric procedure has been described for the determination of trace amounts of endosulfan (an organochlorine pesticide) using static mercury drop electrode. The developed procedure is very sensitive (0.07 to 1.43 ppm) with a detection limit of 14 ppb. It has been used for the determination of endosulfan in formulations and tomato samples in aqueous ethanolic medium.

Endosulfan (thiodan) a broad spectrum chlorinated insecticide containing sulphur is effective against many types of pests of plants and vegetables. The most suitable technique for the determination of endosulfan, an organochlorine pesticide, is gas chromatography with electron capture detection, although GC-MS, liquid chromatography, TLC and spectrophotometric and electroanalytical techniques have also been used. Electroanalytical techniques based on polarography are generally not very sensitive but Prabhu and Manisankar who investigated differential pulse and square wave stripping voltammetric techniques using glassy carbon electrode and found that the latter technique is more sensitive for the determination of endosulfan (0.07-0.26 ppm). The present note describes a differential pulse anodic stripping voltammetric procedure for the determination of as low as 14 ppb of endosulfan in aqueous ethanolic medium using static mercury drop electrode. The developed procedure has been successfully utilized for the determination of endosulfan in formulations and vegetable samples.

Experimental
A stock solution of endosulfan (10⁻² M) was prepared by dissolving 0.4154 g of the sample obtained commercially (United Phosphorus Limited, Bombay) in 100 ml of ethanol. Ammonium acetate (1 M) was prepared by dissolving 7.708 g of the sample in 100 ml of distilled water. Stripping voltammograms were recorded with a Princeton Applied Research Model 174 system with a Model 303 static mercury drop electrode (SMDE). Deaeration was done with purified nitrogen. The reference electrode was Ag-AgCl with an auxiliary Pt electrode. The recordings were made on a RE 0074 XY/T recorder.

General procedure
An aliquot of sample solution containing 5x10⁻⁷ - 10⁻³ M (6 ml) endosulfan was transferred to a 10 ml volumetric flask. Ammonium acetate (1 ml) and ethanol (3 ml) were added to it and the volume was made up with water. The solution was transferred into the electrochemical cell in which SMDE was placed. After deaeration, deposition was allowed for 2 min at -1.2 V vs Ag-AgCl. Turbulence was allowed to cease (30 s) and the potential was anodically scanned from -1.2 to 0.0 V with a scan rate of 2 mV/s and a pulse amplitude of 25 mV.

Results and discussion
Differential pulse polarographic studies revealed that a clear peak occurred at -1.16 V Ag-AgCl due to the 2 electron reduction involving the removal of chlorine atom followed by the addition of hydrogen. In aqueous ethanolic medium endosulfan gave an oxidation peak at a potential of about -0.53 V in 0.1 M ammonium acetate when DPASV was scanned. The determination of 5x10⁻⁶ M endosulfan was studied in the presence of different supporting electrolytes and it was found that ammonium acetate gave maximum Ip values and hence it was chosen for further studies. In order to ascertain the optimum
deposition potential \( (E_d) \) the cathodic limit of the deposition potential was varied in the range -1.5 to -1.0 V vs Ag-AgCl in steps of 0.1 V. The stripping signal was constant and maximum at potentials ≥ -1.1 V and hence -1.2 V was chosen in subsequent studies. The effect of deposition time on the magnitude of stripping signal from 60 to 600s was studied. The stripping signal was found to be linear with time of deposition. A deposition time of 20s was chosen as it offers reasonable sensitivity.

The effect of scan rate in the range, 1.0 to 100 mV was studied during DPASV determination of endosulfan. At scan rates ≤ 2 mVs the sensitivity was found to be best and hence this rate was chosen for further work. The modulation amplitude was varied from 5 to 100 mV. There was no change in sensitivity in the modulation amplitude range of 25-100 mV, and hence 25 mV was chosen for all further studies. The influence of other co-existing interfering agents on DPASV determination of endosulfan was studied. It was found that 10-fold amounts of DDT, BHC, methyl parathion, ziram, thiram and propoxur do not interfere in the determination of endosulfan. The DPASV signal was found to be linear in the range of \( 5 \times 10^{-7} \) to \( 10^{-5} M \) of endosulfan with a detection limit of 14 ppb. The coefficient of variation for \( 10^{-7} M \) of endosulfan was found to be 2.3% for five successive determinations.

**Analysis of tomato samples**

Tomato extracts were prepared by extracting 50 g sample in 80 ml of ethanol by heating. The solution was filtered and the volume was made up to 100 ml. Aliquots of the sample were used for analysis. A blank was also run to check whether there were any interferences present at the same current signal. From the results (Table 1) it is evident that the developed DPASV procedure could be reliably used for the determination of endosulfan in tomato samples.

**Analysis of formulations**

50% wettable formulation of Endosulfan available as Thiokill in local market was analysed for endosulfan content. The sample was dissolved in ethanol and volume was made upto 100 ml. Suitable aliquots of the sample were used for analysis. The results agree with the certified percentage of endosulfan (Table 1).

**Acknowledgement**

One of the authors (LM) is grateful to CSIR, New Delhi for the award of Research Associateship.

**References**


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**Table 1 - Determination of endosulfan in tomato samples and formulations**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of endosulfan added (µg)</th>
<th>Certified amount (%)</th>
<th>Amount found* (mg)</th>
<th>Recovery (%)</th>
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<tr>
<td>Tomato**</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>5</td>
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<tr>
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<td>10</td>
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<td>9.9</td>
<td>99.0</td>
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<td>Formulation</td>
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<td>50</td>
<td>49.5***</td>
<td>99.0</td>
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</table>

*Mean of three replicate; **Amount of sample -50 g;***Amount found (%)