

Figure 2: Typical DPP Polarograms for Thiophanate methyl (in absence of Triton-X) at DME

oxidisable behaviour at DME, working electrode using tetraethylammonium perchlorate (TEAP) as supporting electrolyte in acetonitrile medium. It is, however, interesting to observe that when thiophanate-methyl is added

incrementally in presence of 0.1% Triton-X-100 (surfactant) and reaction studied quantitatively at DME, diffusion-controlled peak shifted slightly towards negative potential and appeared at 140 mV (Figure 3) with

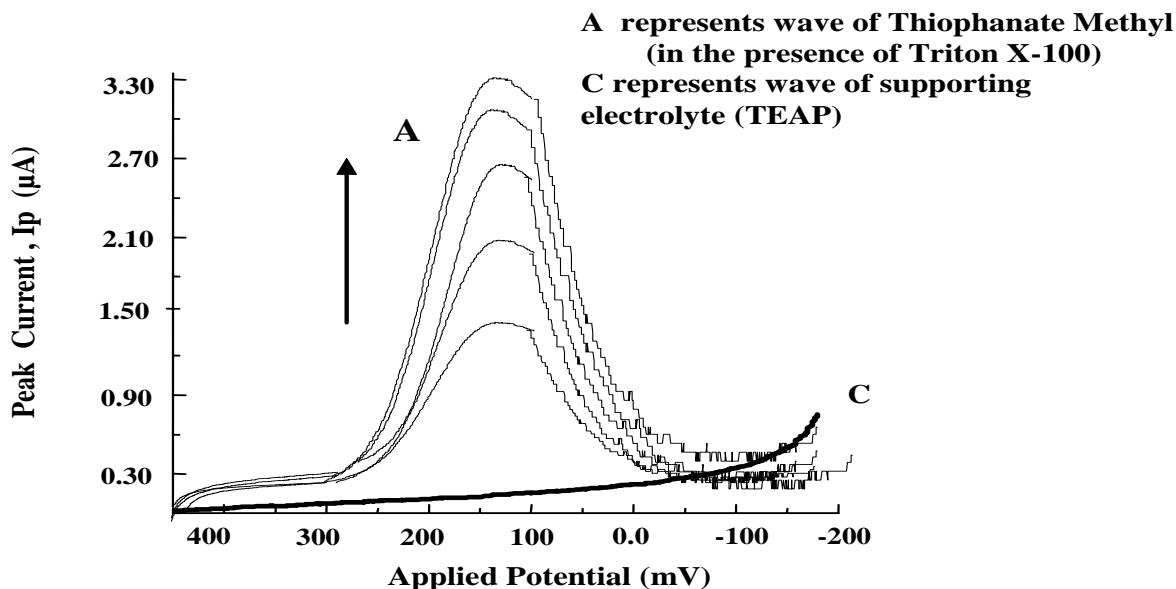


Figure 3: Typical DPP Polarograms for Thiophanate methyl (in presence of Triton-X) at DME

enhanced sensitivity in terms of peak current height and sharpening of peak. Electrochemical characteristics obtained during DPP studies of thiophanate-methyl solution listed in Table 2.

The remarkable sensitivity of the new peak at 140 mV coupled with the excellent linear relationship obtained between concentration of thiophanate-methyl added and current intensity of anodic peak provides a sensitive differential pulse polarographic method for the determination of thiophanate-methyl (Figure 4).

Table 2: Electrochemical characteristics of thiophanate-methyl solution at DME during differential pulse polarographic (DPP) studies

| Characteristics | Differential pulse polarographic (DPP) studies at DME | |
|------------------------------------------------------|-------------------------------------------------------|-----------------------------------------------|
| | In Acetonitrile (In absence of Triton -X-100) | In Acetonitrile (In presence of Triton-X-100) |
| Peak Potential , E_p (mV) | 150 | 140 |
| Half wave Potential, $E_{1/2}$ (mV)= E_p (mV)-50/2 | 125 | 115 |

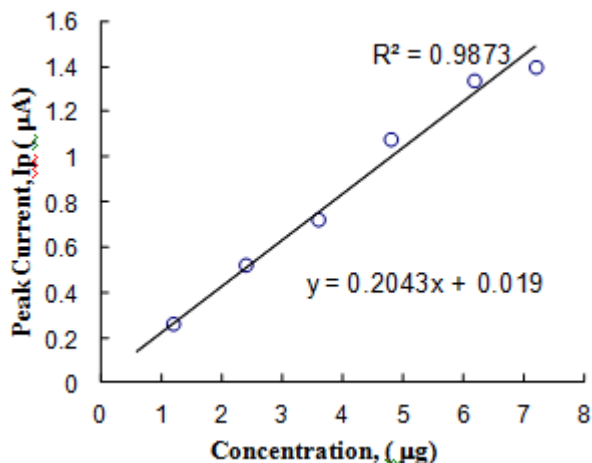


Figure 4: Calibration graph for Thiophante methyl in presence of Triton X-100 at DME

The method has successfully been applied to both commercial fungicide formulation and agricultural produces

3.2 Effect of Solvent and supporting electrolyte

Determination by non-aqueous polarography is advantageous as thiophanate-methyl shows poor solubility in water but it also undergoes decomposition in an aqueous medium containing acids or bases (commonly employed in aqueous polarography in the form of acidic/basic buffer or acidic/alkaline electrolytes). Acetonitrile has been a solvent of choice in the present studies because of its convenient liquid range, ready availability, wide electrochemical range, moderate dielectric constant (facilitating the solubility of this compound) and low toxicity. Since the solvent and supporting electrolyte can significantly affect the redox properties and voltammetric responses, the choice of proper solvent-electrolyte system becomes all the more important [18],[19]. Among the various supporting electrolytes such as lithium chloride, sodium perchlorate, tetrabutylammonium iodide studied, TEAP has been found suitable supporting electrolyte in acetonitrile. Using this system, a linear base line having a plateau parallel to the potential axis was obtained over quite a wide range of potential. The polarographic behavior of thiophanate-methyl and formulated product based on it, in the presence of Triton-X-100 at DME yielded well defined, more sensitive diffusion-controlled peak at 140 mV against SCE electrode at.

3.3 Effect of surfactant - Triton-X-100

In the present study Triton-X-100 was selected because of its capability to suppress the undesirable peaks of impurities and to prevent adsorption of oxidation products which generally interfere in analysis. Secondly, addition of optimized levels of Triton-X-100 is also reported to sharpen and increase the height of the analyte peak with slight shift in peak potential [20]. Figure 5 shows the results obtained for the peak current for different

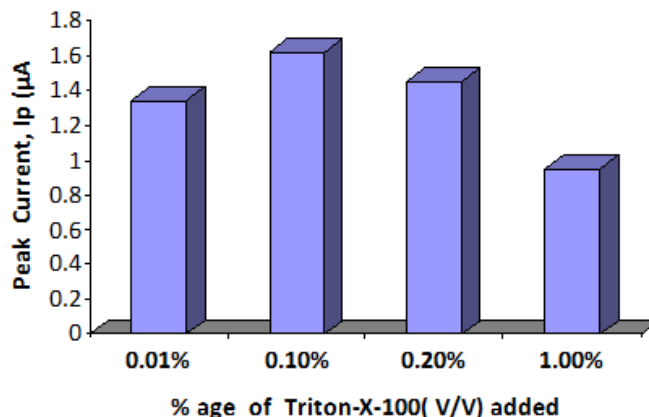


Figure 5: Dependence of the peak current (I_p) on the % age (V/V) of Triton-X-100 for a thiophante methyl solution at concentration level of 8 µg/mL

%age of Triton X-100 (V/V) added to the solution. It was possible to use high concentrations of Triton without problems of foam formation. For low percentages of Triton, adsorption effects occur and the reproducibility was not good; at high percentages greater adsorption of the surfactant itself on the electrode surface caused diminution of the peak current, but good reproducibility was obtained. Addition of 0.1% Triton to the solution was found to be most suitable and in these optimized conditions. Similar results were obtained in present study due to apparently facilitating the oxidation mechanism and producing an associated increase in the peak height.

3.4 Validation of Proposed Method

3.4.1 LOD and LOQ

According to International conference on Harmonization (ICH) guidelines, following expressions are applied to evaluate limit of detection (LOD) and limit of quantitation(LOQ): $LOD = 3 SD/b$ and $LOQ = 10 SD/b$ where SD is standard deviation of intercept and b is slope of regression line. The calculated LOD and LOQ are found to $0.1 \times 10^{-6}g$ and $0.3 \times 10^{-6}g$ respectively as shown below in the Table 3.

Table 3: Calibration characteristics of thiophanate-methyl solution in the presence of Triton-X-100 at DME during differential pulse polarographic (DPP) studies

| Characteristics | Values |
|--------------------------------|-----------------------|
| LOD | $0.1 \times 10^{-6}g$ |
| LOQ | $0.3 \times 10^{-6}g$ |
| Linear range, µg/mL | 0.5-16 |
| Slope | 0.2043 |
| Intercept | 0.019 |
| Correlation coefficient, R^2 | 0.9873 |

3.4.2 Specificity

Specificity is ability of any analytical method to measure analytical response in the presence of all possible and potential impurities. For such test, DPP voltammogram of standard solution of commercial formulation excipients (additives) were recorded. Such additives exhibited no electroanalytical response in applied controlled potential range. Response of analyte in presence of excipients was compared with standard pure thiophante methyl and found to be stable.

3.4.3 Stability

In the this voltammetric study, standard of pure thiophante methyl stock solution was kept in dark at 4°C for 20 days in refrigerator and were analyzed at every day (at different time). Reproducibility of peak current of stock solution of thiophante methyl was observed for 10 days and after that peak current decreased significantly.

3.4.5 Application of the proposed method

Electroanalytical peak at 140 mV appeared in the voltammetric study has been exploited and made the basis of the proposed differential pulse polarographic method. The method has been successfully applied to the analysis of a formulation of thiophanate-methyl for its active ingredient content. The recoveries were the range 97.6-101 % with RSD's in the range 0.64-0.88 % for formulation analysis (Table 4).

Table 4: Assay of a commercial formulation of thiophanate-methyl containing 70% active ingredient

| Active ingredient taken (µg) | Mean peak Current obtained, I _p (µA) | Amount found (µg) | Recovery ^a (%) |
|------------------------------|-------------------------------------------------|-------------------|---------------------------|
| 0.5 | 0.119 | 0.49 | 98.0 ± 0.78 |
| 1.0 | 0.183 | 0.98 | 98.0 ± 0.67 |
| 2.0 | 0.385 | 1.98 | 99.0 ± 0.64 |
| 4.0 | 0.844 | 4.04 | 101 ± 0.74 |
| 8.0 | 1.612 | 7.80 | 97.5 ± 0.70 |
| 16.0 | 3.188 | 15.70 | 98.12 ± 0.88 |

^aValues are mean of five determinations with relative standard deviations (±)

Recoveries of the fungicide from fortified grain samples (wheat and rice) and apple fruit were good, ranging from 88.8-98.4% with RSD's in the range 0.69-0.98 % (Table 5).

Table 5: Recovery of thiophanate-methyl from fortified samples

| Active ingredient added (µg) | Recovery ^a (%) | | |
|------------------------------|---------------------------|-------------|-------------|
| | Wheat | Rice | Apple |
| 2.0 | 94.2 ± 0.69 | 96.6 ± 0.92 | 92.2 ± 0.98 |
| 3.0 | 97.8 ± 0.94 | 97.0 ± 0.72 | 89.8 ± 0.87 |
| 6.0 | 98.4 ± 0.80 | 95.8 ± 0.78 | 90.8 ± 0.80 |
| 12.0 | 95.6 ± 0.79 | 98.2 ± 0.84 | 92.4 ± 0.96 |
| 14.0 | 96.4 ± 0.75 | 92.8 ± 0.86 | 94.2 ± 0.72 |

^aValues are mean of five determinations with relative standard deviations (±)

4. Conclusions

In our efforts to explore the electroanalytical aspects using voltammetry, we found differential pulse polarography as an emerging and remarkably sensitive technique for determination of thiophanate methyl. The electrochemical response of thiophanate-methyl facilitated in presence of Triton X -100 (0.1% V/V) at the DME electrode surface in term of enhanced peak current and sharpening of diffused controlled peak at 140 mV.

The simplicity and rapidity (due to non requirement of extraction apparatus for colored product, a common practice in colorimetric analysis) of the procedure: remarkable sensitivity of the technique and its use for both formulation

and agricultural produces are significant advantages, which the method possesses over the colorimetric methods. That the method is indeed reproducible is evident from the good precision data (in terms of RSD's) obtained in the analysis of the fungicides.

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Author Profile



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