Differential pulse polarographic determination of tetramethylthiuram disulphide

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A differential pulse polarographic method for the determination of tetramethylthiuram disulphide (TMTD) by making use of its reaction with copper(I) perchlorate in acetonitrile has been developed. TMTD reacts with copper(I) perchlorate (1:1 molar ratio) and exhibits a well-defined, diffusion-controlled peak at -120 mV showing five times more sensitivity than the one obtained due to TMTD alone. The linear relationship between concentration of TMTD and current intensity of peak at -120 mV can be successfully adapted to the analysis of some fungicide and rubber accelerator formulations based on TMTD.

In view of the wide use of tetramethylthiuram disulphide (TMTD) as an agricultural fungicide (thiram) and rubber accelerator (methyl tuad/thiurad), there is dire need of a sensitive method for its analysis. That pulse polarography has emerged as a reliable and sensitive tool for trace analysis, is now quite well known. In a significant effort in this context, we have been able to work out a remarkably sensitive method for the determination of TMTD by making use of its reaction with copper(I) perchlorate in acetonitrile. The method is based on the above reaction by using dropping mercury electrode (DME) as the working electrode, saturated calomel electrode (SCE) as reference electrode, platinum wire as an auxiliary electrode and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte. Copper(I) perchlorate (in acetonitrile) gives a well-defined, diffusion-controlled reduction peak at -290 mV. TMTD gives a similar peak at 260 mV. It is, however, interesting to observe that when copper(I) is added incrementally to TMTD and the reaction studied quantitatively, whereas copper(I) and TMTD peaks at -290 mV and 260 mV, respectively exhibit decrease in their current intensity, a new diffusion-controlled peak appearing at -120 mV shows a proportional increase in current intensity. This trend continues till copper(I)-TMTD molar ratio 1:1 is achieved. At this point, whereas both copper(I) and TMTD waves disappear completely, the new peak at -120 mV shows its maximum current intensity. The new peak at -120 mV shows approximately five times more sensitivity than the one due to TMTD alone. The remarkable sensitivity of the new peak coupled with the excellent linear relationship obtained between concentration of TMTD added to copper(I), and current intensity of this peak provides a sensitive pulse polarographic method for the determination of TMTD. The method can be adapted to the analysis of commercial fungicide and rubber accelerator formulations.

Experimental
Acetonitrile (Merck) was kept over phosphorus pentoxide (5 g L-1) and distilled twice. Tetraethylammonium perchlorate was prepared by a reported method1. Its standard solution was prepared by dissolving 2.296 g of pure compound in one litre of acetonitrile. The analytical standard of tetramethylthiuram disulphide (Fluka, Switzerland) was used. Its stock solution (10-3 M) was prepared in acetonitrile. Copper(I) perchlorate was prepared by a known method2. Its standard solution (0.001 M) was prepared by the method reported earlier2. Triton X-100 (Merck), 0.002% in acetonitrile, was used as a suppressor. All polarographic measurements were made with an Elico (India) pulse polarograph (model CL-90) equipped with DME as working electrode, SCE as reference electrode and a coiled platinum wire as an auxiliary electrode.

5.0 mL each of copper(I) perchlorate and TMTD (each 0.001 M in acetonitrile) were taken separately in 50 mL glass stoppered flasks and diluted to 20 mL with acetonitrile, mixed with 20 mL of tetraethyl ammonium perchlorate (0.01 M in acetonitrile). Triton X-100 (2 mL, 0.002% in acetonitrile) was added as suppressor and the final volume made to 50 mL with tetraethyl ammonium perchlorate. Nitrogen gas was passed through each solution for 5 min. The differential pulse polarogram of each solution was recorded at room temperature (23 ± 1°C) with following instrumental parameters: Initial potential = +400 mV; drop time = 1 s; pulse amplitude = 50 mV; sensitivity = 1 µA/V; X-axis = 100 mV/cm and Y-axis = 260 mV.
= 200 mV/cm (on polarocord). Typical differential pulse polarograms of copper(I) perchlorate and TMTD are shown in Figs 1 and 2.

Preparation of calibration graph for TMTD
Aliquots (0.1-2.0 mL) of the stock solution of TMTD in acetonitrile were taken in polarographic cells containing 5.0 mL of copper(I) perchlorate (0.001 M in acetonitrile) and volume made to 20 mL with acetonitrile. Triton X-100 (2 mL, 0.002% in acetonitrile) was added and final volume made to 50 mL with tetraethyl ammonium perchlorate (0.01 M in acetonitrile). Nitrogen gas was bubbled through each solution for 5 min and differential pulse polarogram was recorded with the above instrumental parameters. A typical differential pulse polarogram resulting from the reaction of copper(I) perchlorate with TMTD is shown in Fig. 3. Calibration graph was constructed by plotting peak current (μA) (corresponding to -120 mV peak) versus concentration of TMTD (μg) added to copper(I).

Formulation analysis
One fungicide formulation (containing 75 % active ingredient, wettable powder) and two rubber accelerator formulations (each containing 100 % active ingredient) were analyzed. A single large sample of each was weighed, shaken with acetonitrile and filtered. The residue (if any) was washed 2-3 times with acetonitrile. The filtrate and washings were diluted to a known volume with the same solvent. Suitable aliquots of the solution were taken and processed for analysis as described above. The results are given in Table I.

Results and discussion
The proposed pulse polarographic method has in fact emerged during our studies on the mechanism of copper(I)-TMTD reaction in acetonitrile. This reaction had afforded us a spectrophotometric method for the determination of thiram based on measurement of yellow colour at 430 nm. Though the stoichiometry of this reaction (1:1 molar ratio) was established, its mechanism, however, continued to grip our mind till we used cyclic voltammetry (CV) to elucidate the same. The CV studies of copper(I)-TMTD reaction in acetonitrile medium using platinum-silver/silver chloride electrode assembly show that TMTD alone does not show any current peak either in forward (negative) or reverse (positive) scan. Copper(I) perchlorate, on the other hand, shows a well-defined peak at 923 mV in forward scan and none in the reverse scan (Fig. 4). Interestingly, however, when TMTD (in acetonitrile) is incrementally added to copper(I) and the progress of copper(I)-TMTD reaction is monitored quantitatively, it is observed that whereas the 923 mV peak shows a
Table 1 — Recovery of TMDT from its commercial products

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Based on active ingredient (%)</th>
<th>Amount taken (µg)</th>
<th>Amount found (µg)</th>
<th>Average recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thirid-75</td>
<td>75</td>
<td>0.24</td>
<td>0.237 ± 0.002</td>
<td>98.8 ± 0.8</td>
</tr>
<tr>
<td>(Fungicide)</td>
<td></td>
<td>0.96</td>
<td>0.952 ± 0.009</td>
<td>99.2 ± 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.92</td>
<td>1.898 ± 0.018</td>
<td>98.9 ± 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.76</td>
<td>5.674 ± 0.042</td>
<td>98.5 ± 0.7</td>
</tr>
<tr>
<td>Methyl Tuad</td>
<td>100</td>
<td>0.40</td>
<td>0.396 ± 0.003</td>
<td>99.0 ± 0.8</td>
</tr>
<tr>
<td>(Rubber accelerator)</td>
<td></td>
<td>1.20</td>
<td>1.181 ± 0.008</td>
<td>98.4 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.20</td>
<td>3.159 ± 0.025</td>
<td>98.7 ± 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.40</td>
<td>6.342 ± 0.046</td>
<td>99.1 ± 0.7</td>
</tr>
<tr>
<td>Methyl Thiurad</td>
<td>100</td>
<td>0.36</td>
<td>0.358 ± 0.003</td>
<td>99.4 ± 0.8</td>
</tr>
<tr>
<td>(Rubber accelerator)</td>
<td></td>
<td>1.08</td>
<td>1.071 ± 0.008</td>
<td>99.2 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.16</td>
<td>2.118 ± 0.015</td>
<td>98.1 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.48</td>
<td>6.402 ± 0.058</td>
<td>98.8 ± 0.9</td>
</tr>
</tbody>
</table>

*Maker specification established by ref. method*

*Average results of three determinations

gradual decrease in current intensity, two new peaks, one at 410 mV in forward scan and the other at 480 mV in reverse scan (showing ΔE value of 70 mV) appear simultaneously and each shows proportional increase in current intensity. This behaviour continues till copper(I)-TMDT molar ratio 1:1 is reached. At this point, whereas the 923 mV peak completely disappears, each of 410 mV and 480 mV peaks attains its maximum current intensity (Fig. 5). On the basis of these CV studies, the reaction between TMDT and copper(I) can be expressed to proceed with the formation of, most plausibly, copper(III) dimethyl dithiocarbamate complex.

$$\text{Me}_2\text{N.CS.S.CS.NMe}_2 + \text{Cu(ClO}_4) \rightarrow [\text{Cu(Me}_2\text{N.CS.S)}_2]\text{ClO}_4$$

The support to the formation of this complex comes from the fact that such complexes are intact synthesized through reaction of copper(I) and thiuram disulphides (a class to which a TMDT belongs). Further, support to the formation of above complex also comes from the observation that when solution obtained on mixing copper(I) and TMDT (each in acetonitrile) in 1:1 molar ratio is reacted with potassium iodide, it liberates iodine indicating that the product formed contains copper not as copper(I) but in its higher oxidation state. With support from the above CV studies, literature citations and experimental observations, it can be inferred that it is this very complex which has generated the new analytically useful peak at -120 mV and has been made basis of the method.

The proposed method is quite sensitive and can be employed for the determination of as little as 0.24 µg ml⁻¹ of TMDT. The relationship between the concentration of TMDT and current intensity (of the
A new peak at -120 mV is found to be linear up to 7.68 µg ml\(^{-1}\) of TMTD. TMTD in the range 2.4-6.4 µg can be determined with a maximum relative standard deviations (RSD's) of 0.92%. The method when applied to the assay of commercial products based on TMTD provides recoveries in the range 98.1-99.4% of the nominal content with RSD's in the range 0.7-0.9% (Table I). The maker's specification of each formulated product has separately been established by an independent method\(^7\).

In the present investigations, acetonitrile has been chosen as the solvent because of the following reasons (i) it is resistant to oxidation or reduction, (ii) it has a high dielectric constant; TMTD is freely soluble in the solvent, and (iii) copper(I) forms a remarkably stable solution in the solvent\(^2,8\).

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References
1. Kolthoff I M & Coezeet J F, Contribution from the School of Chemistry, University of Minnesota, 79.