Chapter VII

3-Methyl-2-benzothiazoline hydrazono hydrochloride hydrate as a new electrophilic coupling reagent for the determination of chloramine-T in environmental water samples
## CHAPTER SEVEN

3-Methyl-2-benzothiazoline hydrazone hydrochloride hydrate as a new electrophilic coupling reagent for the determination of chloramine-T in environmental water samples

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Abstract

A new oxidative electrophilic coupling method was developed for spectrophotometric determination of trace amounts of chloramine-T (CAT) in various environmental water samples. The method is based on the reduction of CAT by electrophilic coupling reagent, 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH), which subsequently couples with trimipramine maleate (TPM) in acidic medium to form blue coloured product having $\lambda_{\text{max}}$ at 630 nm. The colour is stable up to 24 h and obeys Beer's Law in different concentration ranges. The optimum reaction conditions and other important analytical parameters were established to enhance the sensitivity of the proposed method. Interference due to various non-target ions was also investigated. The proposed method can be applied to the analysis of CAT in different environmental water samples. The performance of proposed method was evaluated in terms of recovery tests by standard addition method and the results indicated the proposed method is not significantly different from the reference spectrophotometric method.

Keywords: Chloramine-T; spectrophotometry; determination; environmental water samples; trimipramine maleate
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3-methyl-2-benzothiazoline samples

VII.1. Introduction

Chloramine-T (CAT) is one of the most widely used chemical disinfectants in drinking water system. CAT, as an anti-microbial agent, has had widespread use in a broad range of practices, including medical, dental, food processing and agriculture. It is used as general disinfectant (germicide) [1] in cattle ranches, thus making it a pollutant in waste waters. It also finds use as an analytical oxidant for inorganic species [2–9] and organic compounds [10–17]. It is also being used to bleach materials (textiles and conservation of books), to dye textiles, as a starting material for some compounds and as a laboratory reagent.

Various methods are available for the determination of CAT; most of them are based on titrimetric determinations using iodide [18] or vanadium(II) in acetic acid [19] as titrant and amplication reactions [20]. Flow methods with spectrophotometric detection [21], gas chromatography [22], liquid chromatography [23] and biamperometric [24] have also been employed for the determination of CAT in foodstuffs and environmental samples. In spite of its general use, few studies have been devoted to the determination of CAT. In the present work a simple spectrophotometric method for the determination of CAT in environmental water samples is proposed. The method is based on the use of trimipramine maleate (TPM) as chromogenic reagent in presence of 3-methyl-2-benzothiazoline-hydrazone hydrochloride hydrate (MBTH) as coupling reagent; it can be applied for the determination of chloramine-T (CAT) in environmental water samples.
VII.2. Experimental

VII.2.1. Preparation of reagent solutions

Stock solution (1000 μg ml⁻¹) of CAT (chemical weight of chloramine-T sodium salt, 3-hydrate) was prepared by dissolving a known quantity of CAT in 1 litre of distilled water. Solutions of required strength were prepared by diluting this stock solution with distilled water. Aqueous solution of 0.1% MBTH (w/v) (Aldrich) was prepared by dissolving 100 mg of the compound in 100 ml of distilled water; the solution was stored in an amber bottle to protect from sunlight.

TPM was received as gift sample from Max Pharma, India. Fresh solution of TPM (0.1% w/v) was prepared by dissolving 100 mg of the sample in 100 ml of distilled water. Few drops of 1N H₂SO₄ were used to dissolve the TPM. Solutions of diverse ions were prepared by dissolving their respective salts. All other chemicals used were of Analar grade.

VII.2.2. Apparatus and spectral characteristics

Specord 50 UV-vis spectrophotometer with 1.0 cm silica quartz matched cell was used for measuring the absorbance.

VII.2.3. Procedure

Aliquots of standard solution of CAT, along with 1.0 ml of 1N hydrochloric acid, 1.5 ml of 0.1% (w/v) MBTH, 0.5 ml of 0.1% (w/v) TPM were taken in a series of 25-ml calibrated standard flasks and kept for 30 min at room temperature. Blue coloured solutions were obtained and were made up to the mark with distilled water. The absorbance was measured at 630 nm against a reagent blank prepared under identical conditions but without CAT. Concentration of CAT in test solutions was calculated from the regression equation computed from
the Beer's law data. The concentration of CAT was determined by proposed method and its other optical characteristics are presented in Table VII.1.

VII. 3. Results and discussion

VII. 3.1. Reaction mechanism, optical characteristics and stability

The chemical reaction in the spectrophotometric study involves the reduction of CAT by MBTH and subsequent coupling with TPM in aqueous acidic medium to form blue coloured species, which showed maximum absorbance at 630 nm. The reagent blank showed practically negligible absorbance at this wavelength. All the blue coloured derivatives under the optimized condition were stable up to 24 h (± 2 % variation). The reaction mechanism is represented in Scheme IV.1.

VII. 3.2. Sequence of addition of reagents

During the course of study it was observed that the sequence of addition of reactants also influenced to a great extent the intensity and stability of the colour. Less intense and unstable colour was observed when the sequence of addition was (i) TPM-acid-CAT-MBTH and (ii) CAT-acid-TPM-MBTH. But, the sequence (iii) CAT-acid-MBTH-TPM and (iv) MBTH-acid-CAT-TPM gave more intense and stable blue colour. This was expected as the reaction in sequence (i) and (ii) produced radical cation, while, in sequence of addition in (iii) and (iv) electrophilic substitution reaction was involved. Sequence of addition of (iii) was selected for further spectrophotometric investigations.
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VII. 3.3. Effect of temperature

The colour development was independent of temperature in the range of 20-35° C (room temperature) and gave the most appropriate results at this temperature. At higher temperatures (heating), the absorbance values decreased and this indicates the dissociation of the colour on prolonged heating. Therefore, all the experiments were carried out at room temperature.

VII.3.4. Effect of reaction time

Experiments were conducted to optimize the time in the determination of CAT. It was found that the stability and intensity of blue colour formed in the reaction was not affected after 30 min and remained constant up to 24 h. Therefore, 30 min was found optimum period for the absorbance study.

VII. 3.5. Effect of different acids

The stability and sensitivity of the blue coloured solution depends on the nature and concentration of the acid medium used. In the proposed method the colour was intense in hydrochloric acid medium, whereas intensity of blue colour was less when sulphuric acid, acetic acid and phosphoric acid, were used.

VII. 3.6. Optimization of analytical variables

VII. 3.6.1. Effect of hydrochloric acid

Effect of different concentration levels of hydrochloric acid on the colour development was studied by using 0.5 - 5N hydrochloric acid. Maximum absorbance was observed when 1N was used. However, it was found that the intensity of the coloured product decreased with increasing concentration of hydrochloric acid. Therefore 1N hydrochloric acid was selected for further
studies. The effect of different volumes of 1N hydrochloric acid was studied in the range of 0.5 - 3.0ml. Almost constant absorbance values were obtained throughout the range of hydrochloric acid. Therefore, 1.0 ml of 1N hydrochloric acid was chosen for further studies.

VII. 3.6.2. Effect of MBTH

Different concentration levels of MBTH was studied in the concentration range of 0.01 - 0.15% of MBTH. Blue coloured solution showed maximum absorbance when 0.1% of MBTH was used. Effect of different volumes of MBTH was studied in the volume range of 0.5 - 4.0 ml. Maximum absorbance was observed when 1.5 ml of 0.1% MBTH was used in all the studies.

VII. 3.6.3. Effect of TPM concentration and volume

Concentrations of TPM in the range of 0.025-0.020 % was studied on the reaction product. Constant and maximum absorbance values were observed in the range of 0.5 - 1.5% of TPM. Therefore, 0.1% of TPM was considered as optimum for reaction study. Likewise, the different volumes of TPM were studied in the range of 0.25 - 3.0 ml. Maximum intense colour was observed when 0.5 ml of TPM was used. Therefore, 0.5 ml of 0.1% TPM chosen as standard for Beer's law study.

VII. 3.7. Analytical data

Blue coloured solution obeyed Beer's law when it was in the concentration range of 0.5 - 10 µg ml\(^{-1}\). Molar absorptivity value was \(1.90 \times 10^4\) L mol\(^{-1}\) cm\(^{-1}\). Sandell's sensitivity value as calculated from Beer's law was found to be 0.0370 µg cm\(^{-2}\). Regression analysis of Beer's law revealed
correlation coefficient of 0.9944. Intercept value was 0.0134 and slope value was 0.0652 with proposed method. These are described by a regression equation, \( Y=ax+b \), where \( Y \) is the absorbance of a 1 cm layer, \( a \) is the slope, \( b \) is the intercept and \( x \) is the concentration of the CAT in \( \mu g \) ml\(^{-1}\) by the least square method. The reproducibility was studied by replicate analysis of a standard CAT solution over a period of 24 h. Other important analytical parameters of CAT are presented in Table VII.1.

**Table VII.1:** Spectral data for the determination of chloramine-T with TPM using MBTH as an electrophilic coupling reagent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>TPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Blue</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>630</td>
</tr>
<tr>
<td>Stability (h)</td>
<td>24</td>
</tr>
<tr>
<td>Beer's law range (( \mu g ) ml(^{-1}))</td>
<td>0.5-10.0</td>
</tr>
<tr>
<td>Molar absorptivity (L mol(^{-1}) cm(^{-1}))</td>
<td>(1.90 \times 10^4)</td>
</tr>
<tr>
<td>Sandell's sensitivity (( \mu g ) cm(^{-2}))</td>
<td>0.0037</td>
</tr>
<tr>
<td>Regression equation*:</td>
<td></td>
</tr>
<tr>
<td>Slope 'a'</td>
<td>0.2607</td>
</tr>
<tr>
<td>Intercept 'b'</td>
<td>0.0134</td>
</tr>
<tr>
<td>Correlation coefficient 'r'</td>
<td>0.9944</td>
</tr>
</tbody>
</table>

*aRegression curve: \( y = ax + b \) where \( x \) is the concentration of chloramine-T in \( \mu g \) ml\(^{-1}\) and \( y \) is absorbance*
VII. 3.8. Effect of diverse ions

To establish the analytical potential of proposed method, the effect of possible interfering ions, which often accompany CAT was examined by the determination of CAT in presence of these ions by the proposed method. An ion was considered to be interfering with the determination if, the obtained absorbance values differed by ±3% from that of CAT alone. As the method is based on the oxidation of MBTH with CAT, strong oxidizing or reducing agents are likely to interfere by the oxidation of MBTH. Metals such as iron(III), vanadium(V), manganese(VII), chromium(VI) and cerium(IV), non metals like bromate, iodate and periodate, residual chlorine, and chloramine-B were found to be interfered severely by lowering the recovery of CAT. However, use of appropriate masking agents could eliminate the interference by these ions. Masking agents like EDTA, tartarate and citrate did not interfered in the determination of CAT. However, if any precipitate was formed during the interference studies, it was removed by centrifugation. The maximum tolerable concentrations of different ions (defined as the foreign-ion concentration causing an error of ±3% for determining the analyte of interest) in the determination of CAT are listed in Table VII.2

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerance limit (µg ml⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi³⁺, Ba²⁺, Ti⁴⁺, EDTA, F⁻, Br⁻, citrate, tartarate, oxalate</td>
<td>200</td>
</tr>
<tr>
<td>Na⁺, Mg²⁺, Al³⁺, Zn²⁺, Pb²⁺, Cd²⁺, K⁺, Hg²⁺, Ni²⁺, CH₃COO⁻</td>
<td>100</td>
</tr>
<tr>
<td>NO₃⁻, Cl⁻, Br⁻, SO₄²⁻, NH₄⁺, CO₂⁺, Cu²⁺, PO₄³⁻</td>
<td>50</td>
</tr>
<tr>
<td>Chloramine-T, Chloramine-B, IO⁻, IO₄⁻, BrO₃⁻, residual chlorine</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table VII.3: Determination of chloramine-T in different environmental water samples by MBTH-TPM method

<table>
<thead>
<tr>
<th>Sample</th>
<th>CAT added (mg/L)</th>
<th>Recovered (mg/L) ± RSD</th>
<th>Proposed method</th>
<th>Reference method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Recovery (%)</th>
<th>t-value&lt;sup&gt;c&lt;/sup&gt;</th>
<th>F-value&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Recovery (%)</th>
<th>t-value&lt;sup&gt;c&lt;/sup&gt;</th>
<th>F-value&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agriculture land water</strong></td>
<td>1.00</td>
<td>0.97 ± 0.52</td>
<td>97.0</td>
<td>0.44</td>
<td>1.25</td>
<td>0.98 ± 0.51</td>
<td>98.0</td>
<td>97.0</td>
<td>1.14</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>4.90 ± 0.29</td>
<td>98.0</td>
<td>0.36</td>
<td>1.34</td>
<td>4.92 ± 0.31</td>
<td>98.4</td>
<td>98.0</td>
<td>1.31</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>7.80 ± 0.36</td>
<td>97.5</td>
<td>0.23</td>
<td>2.98</td>
<td>7.88 ± 0.24</td>
<td>98.5</td>
<td>98.0</td>
<td>2.31</td>
<td>2.98</td>
</tr>
<tr>
<td><strong>Cattle ranches waste water</strong></td>
<td>1.00</td>
<td>1.03 ± 0.48</td>
<td>103.0</td>
<td>0.53</td>
<td>1.64</td>
<td>1.02 ± 0.62</td>
<td>102.0</td>
<td>102.0</td>
<td>1.64</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>5.10 ± 0.20</td>
<td>102.0</td>
<td>0.61</td>
<td>1.31</td>
<td>5.12 ± 0.47</td>
<td>102.4</td>
<td>102.4</td>
<td>1.31</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>8.15 ± 0.26</td>
<td>101.8</td>
<td>0.81</td>
<td>2.98</td>
<td>8.17 ± 0.58</td>
<td>102.1</td>
<td>102.1</td>
<td>2.98</td>
<td>2.98</td>
</tr>
<tr>
<td><strong>Lake water</strong></td>
<td>1.00</td>
<td>0.98 ± 0.54</td>
<td>98.0</td>
<td>0.36</td>
<td>2.31</td>
<td>0.97 ± 0.43</td>
<td>97.0</td>
<td>97.0</td>
<td>2.31</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>4.92 ± 0.75</td>
<td>98.4</td>
<td>0.88</td>
<td>2.27</td>
<td>4.86 ± 0.24</td>
<td>97.2</td>
<td>97.2</td>
<td>2.27</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>7.88 ± 0.95</td>
<td>98.5</td>
<td>0.30</td>
<td>2.11</td>
<td>7.82 ± 0.19</td>
<td>98.0</td>
<td>98.0</td>
<td>2.11</td>
<td>2.11</td>
</tr>
<tr>
<td><strong>Sewage water</strong></td>
<td>1.00</td>
<td>0.97 ± 0.42</td>
<td>97.0</td>
<td>0.21</td>
<td>1.55</td>
<td>0.97 ± 0.32</td>
<td>97.8</td>
<td>97.8</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>4.85 ± 0.34</td>
<td>97.0</td>
<td>0.29</td>
<td>1.28</td>
<td>4.86 ± 0.18</td>
<td>97.2</td>
<td>97.2</td>
<td>1.28</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>7.80 ± 0.63</td>
<td>97.5</td>
<td>0.64</td>
<td>2.10</td>
<td>7.82 ± 0.54</td>
<td>97.8</td>
<td>97.8</td>
<td>2.10</td>
<td>2.10</td>
</tr>
</tbody>
</table>

<sup>a</sup> - Reference 18, <sup>b</sup> - Average of five-determinations, RSD - relative standard deviation; <sup>c</sup> - Tabulated t-value at 95% confidence level is 1.96; <sup>d</sup> - Tabulated F-value at 95% confidence level is 3.75.

VII. 3.9. Applications

The proposed method was applied in the determination of chloramine-T in environmental water samples collected from sources origins. Environmental samples from agriculture land water, cattle ranches waste water, lake water and sewage water were tested for CAT. The results showed that all the samples tested negative for the presence of CAT. CAT in doped samples collected was determined from three calibration solutions prepared by the standard addition method. These results were compared validated simultaneously with the reference method [18]. The CAT recoveries by the proposed method and the reference
method are shown in Table VII.3. Statistical analysis of the results by Student’s $t$-test and $F$-test indicated no significant difference between the proposed method and reference method.

VII.4. Conclusion

Trimipramine maleate (TPM) is novel as a new spectrophotometric reagent for the determination of chloramine-B in environmental water samples. It exhibits better sensitivity and higher reproducibility. The use of aqueous mild acidic medium makes the procedure cost-effective and versatile. The proposed method has distinct advantages of simplicity, sensitivity, reproducibility and generates lesser amounts of toxic waste.
References


