Chapter V

3-Chloroiminodibenzyl as a novel spectrophotometric reagent for the determination of manganese(VII) in soil, natural water and industrial waste water samples
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Abstract

3-chloroiminodibenzy1 (Cl-IDB) is developed as a novel spectrophotometric reagent for the determination of manganese(VII) in soil, natural water and industrial waste water samples. The reaction method is based on the reduction of manganese(VII) by electrophilic coupling reagent, 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) and subsequent coupling of MBTH with Cl-IDB in acidic medium, which results in the formation of a blue coloured product having \( \lambda_{\text{max}} \) at 660 nm. The colour was stable up to 24 h and obeyed Beer's Law in the concentration range of 0.4-4.0 \( \mu g \text{ ml}^{-1} \). The optimum reaction conditions and other important analytical parameters were established to get maximum sensitivity of the proposed method. Interference by various non-target ions was also investigated. The proposed method was successfully applied for the determination of manganese(VII) in soil, natural water and industrial waste water samples.

Keywords: Manganese(VII); spectrophotometry; 3-chloroiminodibenzy1; 3-methyl 2-benzothiazoline hydrazone hydrochloride hydrate; soil natural water and industrial waste water samples.
V.1. Introduction

Manganese is both a micronutrient as well as toxic element for living beings, depending on the concentration level. The metal plays important roles in biological system. It occurs in domestic wastewaters, industrial effluents and receiving streams. The industrial effluents even after treatment still contain manganese in substantial amounts. Manganese occurs in surface waters both in suspension in the quadrivalent and trivalent state in a relatively stable soluble complex. Higher Concentration in excess of 1 mg L\(^{-1}\) imparts objectionable and tenacious strains to laundry and plumbing acceptable water stream from these rather than toxicological considerations. Although manganese is an essential element for plants and animals, chronic poisoning is sometimes observed in mining industry. Manganese in the air may cause adverse effects on humans [1]. Poisoning takes the form of progressive deterioration in the central nervous system [2]. Manganese contributes to the formation of anterior pituitary hormone, vitamin B\(_1\) and vitamin C affecting hematopoiesis oxidation and proteometabolism in the body. Besides, many enzymes such as dipeptidase, arginase and phosphatase require manganese for their proper functioning. However, excess of manganese in food or pharmaceutics will be hazardous to human health.

Technological developments in the latter part of the present century have placed an increasing demand on chemists and environmentalists to produce analytical techniques, which are cheap (in terms of outlay and running costs), reliable, rapid, simple to operate, accurate, sensitive, amenable to automation, and can be used as portable equipment. Photometric methods are therefore particularly suitable for this. Therefore, in this chapter we report first-ever use of 3-chloroiminodibenzyl
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(Cl-IDB) as chromogen for the determination of manganese(VII) in soil, natural water and industrial waste water samples is reported. The chemical reactions involved have been investigated and the results showed that the method is simple, rapid and sensitive. Besides, Cl-IDB along with MBTH offer clear advantages over most of the chromogenic reagents currently used for the purpose and the procedure claims positive features over the existing methods.

V.2. Experimental

V.2.1. Reagents and apparatus

Stock solution of manganese(VII) (1000 µg ml⁻¹) was prepared by dissolving 0.2873 g of potassium permanganate in 100 ml of distilled water. Cl-IDB was received as gift sample from Max Pharma, India and fresh solution of 0.1% Cl-IDB was prepared by dissolving in distilled ethyl alcohol. Aqueous solution of MBTH (Sigma USA) (0.05% w/v) was prepared by dissolving the same in distilled water. The solutions of MBTH and Cl-IDB are stable for a week under refrigeration and protected from light. Solutions of diverse ions were prepared by dissolving their respective salts. Alcohol was distilled before use. Specord 50 UV-vis spectrophotometer with 1.0-cm silica quartz matched cell was used for recording the absorption spectra and for absorbance measurements.

V.2.2. Procedure

Appropriate volumes of standard solution of manganese(VII), 1.0 ml of 0.5N phosphoric acid, 0.5 ml of 0.0125% (w/v) MBTH and 1.0 ml of 0.1% (w/v) Cl-IDB were added to a series of 25-ml calibrated flasks. The contents were mixed
thoroughly and the solutions were made up to the volume with distilled ethyl alcohol. The absorbance of the resultant blue coloured complex was measured against the corresponding reagent blank at 660 nm. Concentration of manganese(VII) in test solution was calculated from the regression equation computed from Beer's law data as reference. The concentration of manganese(VII) determined and its optical characteristics are presented in Table V.1.

**Table V.1:** Spectral data for the determination of manganese(VII) with Cl-IDB using MBTH as an electrophilic coupling reagent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CI-IDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Blue</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>660</td>
</tr>
<tr>
<td>Stability (h)</td>
<td>24</td>
</tr>
<tr>
<td>Beer's law ($\mu$g ml$^{-1}$)</td>
<td>0.04 - 4.0</td>
</tr>
<tr>
<td>Recommended manganese(VII) concentration ($\mu$g ml$^{-1}$)</td>
<td>0.25</td>
</tr>
<tr>
<td>Molar absorptivity (L mol$^{-1}$ cm$^{-1}$)</td>
<td>$5.8933 \times 10^4$</td>
</tr>
<tr>
<td>Sandell’s sensitivity ($\mu$g cm$^{-2}$)</td>
<td>0.0009</td>
</tr>
<tr>
<td>Regression equation$^a$:</td>
<td></td>
</tr>
<tr>
<td>Slope ‘a’</td>
<td>0.2868</td>
</tr>
<tr>
<td>Intercept ‘b’</td>
<td>0.1452</td>
</tr>
<tr>
<td>Correlation coefficient ‘r’</td>
<td>0.9941</td>
</tr>
</tbody>
</table>

$^a$Regression curve: $y = ax + b$ where $x$ is the concentration of manganese(VII) in $\mu$g ml$^{-1}$ and $y$ is the absorbance
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V.3. Results and discussion

V.3.1. Absorption spectra of coloured derivatives

The absorption spectra values of the blue coloured product were recorded with a Specord 50-UV-vis spectrophotometer by scanning the wavelength in the region of 400-740 nm. Maximum absorption was observed at 660 nm; the reagent blank showed negligible absorption at this wavelength.

Under the optimal conditions, although the colour could develop almost instantaneously, 1 min was allowed to obtain the maximum and constant absorbance in both the methods. The blue colour was stable up to 24 h. The absorbance varied by ±2 % within a day. The colour development was independent of temperature in the range of 20-35°C and gives the most useful results in this temperature range. At higher temperature absorbance values decreased and that indicated the dissociation of colour on prolonged heating.

V.3.2. Temperature and stability

The effect of temperature on the colour formation reaction of manganese(VII) was studied at room temperature. The blue colour developed at room temperature, decreased with increase in temperature. Hence, all experiments were carried out at room temperature. The intensity of the blue colour when diluted with water decreased rapidly, but ethyl alcohol stabilized the colour up to 24 h.

Acids like sulphuric acid, nitric acid and perchloric acid and bases such as sodium hydroxide, ammonia; and solvents like acetone, acetic acid and acetonitrile, did not stabilize the blue colour. As against this, methyl alcohol and ethyl alcohol
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showed profound influence on the stability of colour. Ethyl alcohol was selected for routine analysis as it is nontoxic and cost-effective.

V.3.3. Order of addition

The sequence of addition of reactants is also important as it influences to a great extent the intensity and stability of the coloured product when the sequence of addition (i) Cl-IDB-acid-manganese(VII)-MBTH and (ii) manganese(VII)-acid-Cl-IDB-MBTH gave less intense and unstable colour. But, the sequence of addition (iii) manganese(VII)-acid-MBTH-Cl-IDB and (iv) MBTH-acid-manganese(VII)-Cl-IDB gave more intense and stable blue colour. This was expected as the reactions in sequence of addition (i) and (ii) produced radical cation while electrophilic substitution reaction was involved in (iii) and (iv).

V.3.4. Reaction mechanism

The chemical reaction in the spectrophotometric study of manganese(VII), involves the reduction of manganese(VII) by MBTH and subsequent oxidative coupling of MBTH with Cl-IDB in acidic medium to form a blue coloured product having $\lambda_{\text{max}}$ at 660 nm. The factors affecting the colour development, reproducibility, sensitivity and adherence to Beer's law were investigated by optimizing the analytical variables. A general reaction mechanism for these is proposed in Scheme V.1.
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\[ \text{Substrate - cerium(IV) / manganese(VII)} \]

**Scheme V.1:** Proposed reaction mechanism between MBTH and Cl-IDB
V.3.5. **Optimization of analytical variables**

In order to achieve high sensitivity, selectivity and optimized analytical system for the determination of manganese(VII), various experimental parameters including concentration of reagents, reaction temperature, reaction time and extent of stability were investigated. The operating conditions were optimized by univariate approach. For a fixed concentration of manganese(VII) and MBTH the colour intensity was maximum when 1.0 ml of 0.1% (w/v) Cl-IDB solution was used. Therefore, 1.0 ml of 0.1% (w/v) Cl-IDB is taken as optimum for routine analysis. It was also found that 0.5 ml of 0.0125% (w/v) MBTH solution gave optimum reproducible result.

V.3.6. **Linearity, accuracy and precision**

The linearity of the spectrophotometric method for the determination of manganese(VII) was evaluated under optimum conditions. The calibration curve was linear over the range of 0.04 – 4.0 µg ml⁻¹ of manganese(VII). The minimum detection limit was found to be 0.02 µg ml⁻¹ of manganese(VII). The minimum detection limit shows the lowest concentration of manganese(VII) that can be detected from the background signal with 99% certainty. Other important analytical parameters are presented in Table.V.1.

V.3.7. **Effect of diverse ions**

The interference by foreign ions which are commonly present in soil was studied by proposed method by adding known amounts of foreign species to a solution containing 0.25 µg ml⁻¹ of manganese(VII). The tolerance limit for various ions is defined as the concentration of added ion causing ± 3% relative error for the
manganese(VII) determination. The developed method is based on the oxidation of MBTH with manganese(VII). Therefore, strong oxidizing or reducing agents are expected to interfere during the analysis of manganese(VII). Masking agents like EDTA, fluoride, tartarate and citrate were not interfered. Therefore, 2.0 ml of 2% EDTA was added to mask the interference by different interfering metals. During the interference studies any precipitate formed was removed by centrifugation. The possible interference and the maximum tolerable concentrations are given in Table V.2.

Table V.2: Effect of divorce species in the determination of 0.25 μg ml⁻¹ of manganese(VII)

<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⁺</td>
<td>50</td>
</tr>
<tr>
<td>Fe³⁺, V⁵⁺, Ce⁴⁺, Cr⁶⁺, Residual chlorine, chloramine-T, chloramine-B,</td>
<td>1.0</td>
</tr>
<tr>
<td>IO₃⁻, IO₄⁻, BrO₃⁻,</td>
<td>0.2</td>
</tr>
</tbody>
</table>

V. 3.8. Applications

The proposed method was used for the determination of manganese(VII) content in soil, natural water and industrial waste water samples. The accuracy of the proposed method for the determination of manganese(IV) in soils was checked by reference AAS method and for water samples with a standard method [3]. The results show a good agreement between the manganese content obtained by the proposed and reference methods (Table V.3 and Table V.4).
Table V.3: Determination of manganese(VII) in soil samples

<table>
<thead>
<tr>
<th>Soil</th>
<th>Proposed method (µg ml⁻¹)</th>
<th>Reference AAS method (µg ml⁻¹)</th>
<th>RSD* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>0.63</td>
<td>0.65</td>
<td>1.3</td>
</tr>
<tr>
<td>Deluvial</td>
<td>0.74</td>
<td>0.77</td>
<td>1.7</td>
</tr>
<tr>
<td>Pseudopodzolic</td>
<td>0.92</td>
<td>0.96</td>
<td>2.0</td>
</tr>
</tbody>
</table>

* - Relative standard deviation (n=3)

Table V.4: Determination of manganese(VII) in water samples

<table>
<thead>
<tr>
<th>Water</th>
<th>Proposed method (µg ml⁻¹)</th>
<th>Reference method[3] (µg ml⁻¹)</th>
<th>RSD* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td>0.32</td>
<td>0.30</td>
<td>0.9</td>
</tr>
<tr>
<td>Industrial waste</td>
<td>0.41</td>
<td>0.38</td>
<td>1.2</td>
</tr>
<tr>
<td>Tap</td>
<td>0.08</td>
<td>0.07</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* - Relative standard deviation (n=3)

V.4. Conclusion

The proposed method, for the determination of manganese(IV) besides being simple, inexpensive, sensitive and precise and also has the advantage of determination without the need for extraction or heating. The method does not involve complicated reaction conditions. The proposed oxidative coupling method has significant advantages over other existing methods in terms of simplicity and free from most of the interfering substances. Furthermore, the use of MBTH as an electrophilic coupling reagent and N-substituted dibenzazepines as chromogenic reagents for the determination of manganese(VII) will open up new area of research. A value-addition to this method can be achieved, if the procedure is combined with on-line or at-line system and this is currently under investigation.
References

