Preparation And Characterization Studies of Manganese (II) Complex with azo reagent (Antipyriyl azo 1-Nitroso-2-naphthol) by Spectrophotometric Methods

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Abstract— A new , simple , sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of Manganese (II) .The method is based on the formation of a 2:1 complex with 3-(4'-antipyriyl azo) 1- nitroso-2-naphthol (APAN) as a complexing reagent was developed . The complex has a maximum absorption at 467 nm and $\varepsilon_{\text{max}}$ of 0.25 X 10$^5$ L. mol$^{-1}$. cm$^{-1}$. A linear correlation (0.1 – 2.4 µg. ml$^{-1}$) was found between absorbance at $\lambda_{\text{max}}$ and concentration . The accuracy and reproducibility of the determination method for various known amounts of Manganese (II) were tested . The results obtained are both precise (RSD was better than 0.26 %) and accurate (relative error was better than 0.22 %). The effect of diverse ions on the determination of Manganese (II) to investigate the selectivity of the method were also studied . The stability constant of the product was 0.72 X 10$^6$ L. mol$^{-1}$. The proposed method was successfully applied to the analysis of synthetic mixtures .

Index Term-- Azo dye , Manganese (II) determination, spectrophotometry, antipyriyl azo 1-nitroso-2-naphthol .

INTRODUCTION

Azo dyes represent the single largest chemical class of industrial colorants. They are the most versatile and robust group of synthetic dyes, which cover the full range of shades of colors. The ease of preparation of azo dyes by diazotization and azo coupling reactions and economy of the reaction have led to the synthesis of many dyes in the past. Azo compounds are known to be involved in a number of biological reaction such as inhibition of DNA, RNA and protein synthesis. Heavy metals are grouped within the category of environmental toxins; it is however a fact that many metals to survive. They play significant roles in biological processes, in diseases, as well as in familial amyotrophic lateral sclerosis and others.

Manganese is an essential micronutrient in the human diet. It plays an important role in bone and tissue formation, reproductive functions, and the activation many enzymes used in metabolic processes and it is also required for protein and fat metabolism. It helps to maintain healthy nerves and immune system and to regulate blood. In chemical analysis, there are a number of important techniques used to determine manganese ion, and these techniques, flame atomic absorption spectrometry, solid phase extraction with atomic absorption spectrometry¹, and inductively coupled plasma atomic emission spectrometry, show good sensitivity but is limited because of expensive instrumentation and high cost for routine analysis. In this research, we hope you will determine of micro amounts of Manganese (II) in a simple way and sensitive, dependent on spectral method.

EXPERIMENTAL

I/ Preparation of the reagent (APAN)

The reagent was prepared by coupling 1-nitroso-2-naphthol with diazotate 4-amino antipyrene in alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g of 4-amino antipyrene in 25 mL of ethanol and concentrated hydrochloric acid with 5 mL of distilled water and adding sodium nitrite solution drop wise at (0-5 C⁰). 1.2 g of 1-nitroso-2-naphthol was dissolved in 25 mL of ethanol and 30 mL of 4.0 M from sodium hydroxide were added at (0-5 C⁰). The mixture was left to stand over night. The precipitate was filtered off and recrystallized from ethanol.

II/Preparation of Manganese(II)complex

The complex was prepared by stoichiometric amount from ligand in 100 mL of ethanol then added drop wise with stirring to a stoichiometric amount 2:1 for cobalt salt in 50 mL hot distilled water. The solid product thus formed off, washed with ethanol and dried.

Apparatus

Spectrophotometric measurement were made with Shimadzu UV – visible – 1700 double beam spectrophotometer using 1.00 cm glass cells. Vibrational spectra were recorded on Test scan Shimadzu FTIR 8000 series. Measurements of pH were made using an Hanna H19811-5 pH – meter equipped with a glass – saturated calomel combined electrode. Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus. Conductivity was measured in DMSO (10⁻³) solution with an Alpha digital conductivity model -800. Elemental analysis (C.H.N) were carried out with a EuroEA Elemental Analyser.
**Reagents**

All chemicals used were of analytical grades

Manganese (II) stock solution (100 µg . ml⁻¹)
Prepared by dissolving 0.04585 g of Manganese chloride in 200 ml of distilled water, working standard of Mn (II) solutions were prepared by simple dilution of the appropriate volume of the standard Mn (II) solution (100 µg . ml⁻¹) with distilled water.

3-(4′-Antipyryl azo)-1-Nitroso-2-naphthol (1 mM)
0.0969 g of reagent was dissolved in 250 ml of ethanol.

Foreign ion solutions (10 µg . ml⁻¹)
These solutions were prepared by dissolved an amount of the compound in distilled water completing the volume in a volumetric flask.

**General Procedure**

An aliquot of sample containing 1-25 µg of Mn(II) was transfer into a series of 10 mL standard flask. 2 mL of 1 Mm of APAN was added and pH was adjusted to 9. The complexes formed were solubilized in water and diluted up to 10 mL in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition.

**Results and Discussion**

**Properties of (APAN) and its metal chelate**

APAN is a tridentate with coordination of azo group nitrogen, hydroxyl group and carbonyl group; it has the following structure in Scheme.1:

![Scheme 1. Structure of APAN](image-url)

Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates. APAN and its metal chelates can be easily solubilized in an aqueous solution. Elemental analyses were carried out on the resulting compound (C% calc. 65.11 ; found 64.46, H% calc.4.42 ; found 4.15, N% calc.18.08 ; found 17.99 )⁽¹⁾. (m.p 203 °C)

**Spectra**

The result of this work indicated that the reaction of Mn (II) with APAN at pH yield highly soluble product which can be utilized as a suitable assay procedure for Mn (II). This product has a maximum absorption at 467 nm Fig. 1 was adopted in all subsequent experiments.
utilized as a suitable assay procedure for determination of Mn(II)). This coloured complex have maximum absorption at 467 nm for Mn(II), the blank at this wavelength shows zero absorbance (Fig. 1). The effect of various parameters on the absorption intensity of the formed products was studied and the reaction condition were optimized. The bands appearing in the range of 226-307 nm are attributed to π→π* transition. The other band observed in the region of 467 nm for Mn(II) is attributed to n→π* electronic transition, that is in accordance with octahedral geometry of Manganese metal ion \(^{14,15}\).

Effect of pH

The pH of metal complex solutions was adjusted using dilute solutions (0.05M) NaOH and (0.05 M) HCl, and the effect on absorbance was studied Fig. 2. The absorbance of the complex was maximum and constant in the pH range given in Table I.

![Fig. 2. Effect of pH](image)

Table I

Analytical characteristics of Mn (II) – complex.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Mn (II) – complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maximum (nm)</td>
<td>467</td>
</tr>
<tr>
<td>Beer’s law range (ppm)</td>
<td>(0.1– 2.4)</td>
</tr>
<tr>
<td>pH range</td>
<td>(7 – 9)</td>
</tr>
<tr>
<td>Sandell’s sensitivity μg . cm(^{-2})</td>
<td>0.00217</td>
</tr>
<tr>
<td>Molar absorptivity (L. mol(^{-1}) . cm(^{-1}))</td>
<td>0.25 X 10(^5)</td>
</tr>
<tr>
<td>Stability constant (L. mol(^{-1}))</td>
<td>0.72 x 10(^6)</td>
</tr>
<tr>
<td>Melting point for reagent</td>
<td>(199 – 201) C (^0)</td>
</tr>
<tr>
<td>Melting point for Mn (II) – complex</td>
<td>(232 - 234) C (^0)</td>
</tr>
</tbody>
</table>

Effect of (APAN) concentration

Various concentration of 3-(4- antipyriyl azo) 1-nitroso-2-naphthol was added to fixed concentration of Mn (II) 3 ml of 1 mM (APAN) solution was sufficient and gave
minimum blank value was increased causing a decrease in the absorbance of the sample. Therefore 3 ml of 1 mM of APAN was used in all subsequent experiment Fig. 3.

Effect of reaction time

The colour intensity reached a maximum after the Mn (II) has been reached immediately with APAN and became stable after one minute, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for a least 24 hours Fig 4.

Effect of temperature

The effect of temperature on the colour intensity of the product was studied. In practice, the same absorbance was obtained when the colour was developed at room temperature (10 – 40) °C, but when the volumetric flask were placed in a water – bath at (50 – 70) °C a loss in colour intensity and stability were observed, therefore it is recommended that the colour reaction should be carried out at room temperature for complex Fig 5.
Calibration graph

The calibration equation for \((0.1 – 2.4 \mu g \text{ml}^{-1}) \text{Mn (II)}\) is:

\[
Y = 0.4604X + 0.0008 \quad (R^2 = 0.9976)
\]

Since the coloured complex is stable for 24 hrs, the method can be applied to large series of samples. The molar absorptivity and sandell’s sensitivity are given in Table.1.

Composition of the complex

The composition of the complex was studied in the excess of reagent solution by the mole-ratio and Job’s methods Fig 6,7. A break at a 1:2 (M:L) mole ratio suggested the formation of complex where \(M=\text{Mn(II)}\) and \(L=\text{APAN}\) under the given condition\(^{16,17}\).

Fig. 5. Effect of temperatures on complex Mn[APAN]₂

Fig. 6. mole-ratio method for Mn[APAN]₂ complex
Conductivity measurements

The solubility of the complex in dimethyl sulfoxide and ethanol permitted the molar conductivity of $10^{-3}$ M solution at 25 °C and by comparison, the electrolytic nature for complex. The low values of the molar conductance data listed in Table II indicate that the complex is non electrolyte.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductivity, S. mole$^{-1}$ cm$^2$ DMSO</th>
<th>Molar conductivity, S mole$^{-1}$. cm$^2$ Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (APAN)</td>
<td>15.12</td>
<td>18.33</td>
</tr>
</tbody>
</table>

Interferences

The effect of diverse ions in the determination metal ion was studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. The metal ion can be determined in the presence of a 8 or more fold excess of cation and anion Table III In the experiment, a certain amount of standard Mn (II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. It is found that all the studied ions interfere seriously. However, their interferences are masked efficiently by addition 1.0 ml of 0.1 M of (KCl).
Table III  
Effect of foreign ions

<table>
<thead>
<tr>
<th>Seq</th>
<th>foreign ions</th>
<th>Conc. μg/ml</th>
<th>E%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hg$^{2+}$</td>
<td>10</td>
<td>+32.12</td>
</tr>
<tr>
<td>2</td>
<td>Cd$^{2+}$</td>
<td>10</td>
<td>+34.52</td>
</tr>
<tr>
<td>3</td>
<td>Fe$^{3+}$</td>
<td>10</td>
<td>+15.43</td>
</tr>
<tr>
<td>4</td>
<td>Zn$^{2+}$</td>
<td>10</td>
<td>+14.21</td>
</tr>
<tr>
<td>5</td>
<td>Pd$^{2+}$</td>
<td>10</td>
<td>+30.91</td>
</tr>
<tr>
<td>6</td>
<td>Cu$^{2+}$</td>
<td>10</td>
<td>+38.61</td>
</tr>
<tr>
<td>7</td>
<td>Ni$^{2+}$</td>
<td>10</td>
<td>+29.33</td>
</tr>
<tr>
<td>8</td>
<td>SO$_4^{2-}$</td>
<td>10</td>
<td>+19.05</td>
</tr>
<tr>
<td>9</td>
<td>CO$_3^{2-}$</td>
<td>10</td>
<td>+1.34</td>
</tr>
<tr>
<td>10</td>
<td>Br$^{-}$</td>
<td>10</td>
<td>+0.89</td>
</tr>
<tr>
<td>11</td>
<td>Cl$^{-}$</td>
<td>10</td>
<td>+0.8</td>
</tr>
<tr>
<td>12</td>
<td>F$^{-}$</td>
<td>10</td>
<td>+3.21</td>
</tr>
<tr>
<td>13</td>
<td>S$_2$O$_8^{2-}$</td>
<td>10</td>
<td>-0.33</td>
</tr>
</tbody>
</table>
**FT.IR of reagent and its complex**

The FT.IR of the free ligand and its metal chelate were carried out in the (400-4000) cm\(^{-1}\) range. The IR bands of the (APAN) and its Mn (II) complex with their probable assignment are given in Table.4. The IR spectrum of ligand shows a broad band at 3425 cm\(^{-1}\), which can be attributed to the naphtholic OH group. However, the \(\nu(N=N)\) stretching band in the free ligand is observed at 1535 cm\(^{-1}\). This band is shifted to lower with low intensity at 1512 cm\(^{-1}\) frequency value upon complexation suggesting chelation via the (M-N) \(^{18}\). The IR spectrum of the ligand revealed a sharp band at 1650 cm\(^{-1}\) due to \(\nu(C=O)\) of pyrazole azo. This band is shifted to higher with low intensity at 1671 cm\(^{-1}\) frequency value upon complexation. The bonding of oxygen to the metal ion is provided by the occurrence of band at 449 cm\(^{-1}\) as the result of \(\nu(M-O)\) \(^{19,21}\).

Table IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu (OH))</th>
<th>(\nu (C=N))</th>
<th>(\nu (C-H))</th>
<th>(\nu (N=N))</th>
<th>(\nu (C=C))</th>
<th>(\nu (C=O))</th>
<th>(\nu (M-O))</th>
<th>(\nu (M-N))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>3425 m</td>
<td>1697 s</td>
<td>3062 m</td>
<td>1535 m</td>
<td>1627 s</td>
<td>1650 s</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>[Mn (L)]</td>
<td>3402 m</td>
<td>-</td>
<td>3062 m</td>
<td>1512 m</td>
<td>1645 s</td>
<td>1671 s</td>
<td>449 w</td>
<td>416 w</td>
</tr>
</tbody>
</table>

S: sharp ; m: medium ; w: weak

On the basis of the FT.IR, stoichiometric, and elemental analysis molar conductivity data the structure of complex can be suggested as the following Scheme.2.
Applications

Determination of Mn (II) in practical samples

To determine the accuracy and precision of the method, Manganese (II) was determined at two different concentrations with different interferences ions and masked these ions by using masking reagent. The results are shown in Table 5, indicate that satisfactory precision and accuracy could be attained with proposed method.

Table V

<table>
<thead>
<tr>
<th>Amount taken of Mn (II) p.p.m</th>
<th>Recovery%</th>
<th>RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>99.31</td>
<td>0.41</td>
</tr>
<tr>
<td>1</td>
<td>99.78</td>
<td>0.26</td>
</tr>
</tbody>
</table>

REFERENCES