Iron (III) forms a greenishblue, water soluble complex with 3-hydroxy-l-phenyl-3-methyltriazene in the pH range from 3.1 to 4.5 with an absorbance peak at 625 m\textmu. This reaction has been used for the direct spectrophotometric determination of iron (III) in presence of almost all the commonly associated elements. The system obeys Beer's Law in the concentration range of 1 to 10 p.p.m. of iron. The sensitivity of the colour reaction determined in Nessler tubes is 1 part of iron in 4,500,000 part of solution and on spot plate is 0.1 γ of iron. The formula of the complex has been determined to be Fe R₃ ( R = Reagent ).

The molecular extinction coefficient at 625 m\textmu and the dissociation constant at 34°C have been determined to be 2.8 x 10^3 and 1.156 x 10^{-11} respectively, and the free energy of formation of the complex as -15.3 K cal./mole.
Bamberger et al. (1) have reported that 3-hydroxy-1-phenyl-3-methyltriazene develops an intense greenish-blue colour with ferric chloride. This property has been successfully used in the colorimetric determination of iron (III). Iron (II) does not exhibit any colouration. Almost all the commonly associated diverse ions do not interfere in the direct determination of iron. The formation of iron complex with the reagent is almost instantaneous and is stable for 40 minutes at 34°C. Apart from other reasons, the fading of the colour with time is due to the reducing effect of the reagent which converts iron (III) to iron (II).

The empirical formula of the complex, determined by applying Job's continuous variation method (3) has been found to be $\text{FeR}_2$. It can best be represented by the following chelate structure:

![Chelate Structure](image)

**EXPERIMENTAL**

Standard Iron (III) Solution - 17.875 gms. of pure ferrous ammonium sulphate were oxidised by nitric acid and the volume was made to 1000 ml. It was diluted to give a solution containing 100 p.p.m. of iron.

Reagent Solution - 0.2 g. of the reagent was dissolved in about
2 ml. of rectified spirit and the volume made to 100 ml. with distilled water to give 0.2% w./v. solution of the reagent.

Buffer Solution - 0.25% w./v. sodium acetate solution was used.

Solutions of diverse ions and instruments were the same as described in Section A Part II.

Spectral Characteristics of Iron Complex - A standard iron solution (2 ml.) containing 100 p.p.m. iron was taken in a 50-ml. flask and a 0.25% sodium acetate solution (2.4 ml.) was added so that the pH of the solution after dilution was about 3.5. The reagent solution (10 ml.) was then added and the volume made up to the mark. Absorbance was measured at different wave lengths from 390 to 300 mμ. Water was used as a blank solution, since the reagent solution has no absorbance in the visible range.

Figure 1 shows the absorbance curve of iron complex. It shows peaks at 400, 490, and 625 mμ. The optical density at 625 mμ is maximum. Hence all subsequent measurements were made at this wave length.

Effect of pH - Solutions containing the same concentrations of iron and the reagent were prepared at different pH values and absorbance was measured at 625 mμ. The range of constant absorbance has been found to be between pH 3.1 and 4.5 (figure 2). Below pH 3.0, the solutions were blue coloured, between pH 3.1 and 4.5, greenish blue, and above pH 4.5, violet with slight turbidity. This is indicative of iron complexes of different compositions at different hydrogen ion concentrations.

Reagent Concentration and Mole Ratio - Solutions containing the same concentration of iron and different quantities of the reagent
Figure 1. Spectral characteristics of iron complex, pH 3.5
Figure 2. Effect of pH
were prepared at pH 3.5 to 3.7 and optical densities measured at 625 \, \text{m} \, \mu. \ Figure \ 3 \ shows \ the \ effect \ of \ increase \ of \ moles \ of \ the \ reagent \ per \ mole \ of \ iron \ on \ optical \ density. \ There \ is \ a \ gradual \ rise \ in \ absorbance, \ indicating \ that \ the \ complex \ is \ in \ a \ highly \ dissociated \ form. \ Full \ development \ of \ colour \ is \ ensured \ at \ 1 \ to \ 30 \ ratio \ of \ iron \ to \ the \ reagent.

**Rate of Reaction and Stability of Complex** - The full colour development of the iron complex is almost instantaneous. It is stable for 40 minutes.

**Effect of Temperature on the Reaction** - The colour intensity of iron complex was slightly decreased with the increase in temperature. There was no difference in the absorbance at 25^\circ \text{C} \ and 35^\circ \text{C}. Hence, maintaining the temperature within 10^\circ \text{C} is considered desirable.

**Beer's Law** - Beer's law was obeyed in the concentration range of 1 to 10 p.p.m. of iron. At higher concentrations of iron, a slight turbidity occurs. The molecular extinction coefficient of the iron complex at 625 \, \text{m} \, \mu has been found to be 2.8 \times 10^3.

**Sensitivity of Reaction** - Sensitivity of the reaction was determined in Nessler's cylinders in the usual way and was found to be 1 of iron in 4,500,000 parts of solution. Spot plate sensitivity was found to be 0.1  \gamma \ of iron.

**Formula of the Complex** - The molar composition of the iron complex was investigated by using Job's method of continuous variation (3). The iron content of the final solution was varied between 7.12 \times 10^{-6} \text{M} \ \text{and} \ 5.69 \times 10^{-6} \text{M} \ \text{and pH was kept at}
Figure 3. Reagent concentration and mole ratio
Figure 4 shows the curves obtained by applying this method. The maximum at 6 ml. of the reagent to 2 ml. of equimolar iron indicates the ratio of iron to reagent as 1 to 3. It is likely that different colours of iron complexes below pH 3.0 and above pH 4.5 are indicative of complexes of different compositions. But because of their unstable nature, colorimetric methods for studying their compositions could not be applied.

**Tolerance of Diverse Ions** - The tolerance of diverse ions was studied in the usual manner. Table I records the results obtained.

Qualitative spot testing has shown that lead(II), tin(II), cadmium(II), mercury(II), antimony(III), bismuth(III), titanium(IV), cerium(IV), platinum(IV), thorium(IV), zirconyl, and alkali and alkaline earth metals and common anions do not give any colour reactions with the reagent and thus they are not likely to interfere in the colorimetric determination of iron (III).

Silver (I), gold (III), phosphate and tartrate interfere. Copper

Table I - Tolerance of Diverse Ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Added as</th>
<th>Conc., p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>Sulphate</td>
<td>100</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>&quot;</td>
<td>100</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>&quot;</td>
<td>100</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>Chloride</td>
<td>100</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Sulphate</td>
<td>50</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>&quot;</td>
<td>100</td>
</tr>
<tr>
<td>Al(III)</td>
<td>&quot;</td>
<td>100</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>&quot;</td>
<td>50</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>Chloride</td>
<td>100</td>
</tr>
<tr>
<td>Molybdate</td>
<td>Sodium</td>
<td>10</td>
</tr>
<tr>
<td>Tungstate</td>
<td>&quot;</td>
<td>10</td>
</tr>
</tbody>
</table>

Silver (I), gold (III), phosphate and tartrate interfere. Copper
Figure 4. Job's method - iron complex
gives a slight precipitate with the reagent. Determination of iron can be made by filtering out the copper precipitate from the solution.

DISCUSSION

The dissociation of the complex in solution can be written as:

\[
\begin{align*}
FeR_3 & = Fe^{3+} + 3R^- \\
C & = 0 \quad 0 \quad (\text{Initial concn.}) \\
(1 - \alpha)C & = C \quad 3 \times C \quad (\text{Final concn.})
\end{align*}
\]

\( \alpha \) being the degree of dissociation and \( C \), the concentration of the complex, assuming no dissociation. The dissociation constant \( K \) is given by the equation:

\[
K = \frac{\alpha C (3\times C)}{C (1 - \alpha)} = \frac{27 \times C^3}{1 - \alpha}
\]

The value of \( \alpha \) may be obtained from figure 3 by the following relationship:

\[
\alpha = \frac{E_m - E_s}{E_m} = \frac{0.194 - 0.05}{0.194} = 0.74
\]

where \( E_m \) is the maximum absorbance obtained from the horizontal portion of the curve, when all the iron is present in the form of complex and \( E_s \) is the observed absorbance at the stoichiometric molar ratio of the reagent to iron in the complex (2). The concentration \( C \), of the complex is equal to the total concentration of iron which is \( 7.16 \times 10^{-5} \text{M} \). By substituting these values in the above equation, the value of \( K \) at 34°C comes to \( 1.156 \times 10^{-11} \). Hence, the stability constant \( K \) of the complex is equal to \( 8.65 \times 10^{10} \).
The standard free energy of formation of the complex from iron sulphate and 3-hydroxy-1-phenyl-3-methyltriazene is calculated from the relation $\Delta F^\circ = RT \ln K$ and works out to be $-15.3$ K cal./mole at $34^\circ$C.

References

1. Bamberger and Renauld, Ber., 30, 2283 (1897).