CHAPTER VII

SPECTROPHOTOMETRIC DETERMINATION OF AROMATIC NITRO COMPOUNDS WITH ZINC
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The determination of aromatic nitro compounds depends mainly upon their reduction by suitable reagents. Cheronis and Ma (1) have critically evaluated the methods of analysis of nitro compounds. Very few spectrophotometric methods are available for the determination of nitro compounds (2,3). In aqueous solution, nitrobenzene after reduction with sodium hydrosulphite is determined with 2-naphthol-3-6-disulphonic acid (4). A sensitive qualitative test for aliphatic and aromatic nitro groups was described by Davidson (5). This test involves the use of zinc dust in presence of ammonium chloride as a reducing agent and then the addition of benzoyl chloride and ferric chloride to form a brilliantly coloured complex. A search of the literature shows that no spectrophotometric study of this test has been reported. Therefore, it was decided to utilize this test, after slight modification, for the determination of aromatic nitro compounds.
EXPERIMENTAL

Reagents: Bausch and Lomb Spectronic-20 was used for the spectrophotometric work. Elico pH meter model LI-10 was used for pH measurements. All the reagents were of analytical grade.

Solution of nitro compounds: 1% solution of the organic nitro compound was prepared in iso-propyl alcohol.

Test compounds: Nitro benzene (B.D.H.95%), p-nitro phenol (SISCO), p-nitro toluene (Riedal), p-nitro aniline (Riedel), m-nitrobenzaldehyde (Rearal). No further purification was done.

Solution of ferric nitrate: 5% solution of ferric nitrate was prepared in distilled water.

Solution of ammonium chloride: 10% solution of ammonium chloride was prepared by dissolving 10 gm of ammonium chloride in 100 ml of distilled water.

Buffer solutions were prepared as described by Britton (6).

Procedure

Qualitative investigations: A solution containing 50 μg - 10 mg of the nitro compound was placed in a test tube, and was diluted with ethanol or propanol to 5 ml. A pinch of zinc dust (100 mg) and 1 ml of 10% ammonium chloride were added. After shaking for 5 minutes, the reaction mixture was filtered on Whatman No.42 filter paper 3-4 cm.
To the filtrate was added 1 drop (0.05 ml) of acetyl chloride and 0.2 ml of 5% solution of ferric nitrate. The appearance of violet colour (or pink or other dark colour) shows the presence of nitro group.

Quantitative investigations: A solution containing a known amount of nitro compound 50 μg - 10 mg was placed in a test tube. To this was added zinc dust (100 mg) and 1 ml of 10% NH₄Cl solution. After shaking for 5 minutes. The solution was filtered into a 10 ml volumetric flask on whatman No.42 filter paper 3-4 cm. The residue was washed with 2 ml portions of propanol and transferred to the same filter paper. To the filtrate was added 0.08 ml acetyl chloride and 0.8 ml of 5% ferric nitrate solution. After the colour was developed, the solution was mixed well and allowed to stand for 5 minutes. Then the volume was made up to 10 ml with propanol. The absorbance was taken at the optimum wavelength (e.g. 550 nm for nitrobenzene).
**RESULTS**

Qualitative colour tests: The colours obtained with the test compounds are given in Table 30.

**TABLE 30**

**QUALITATIVE TEST OF NITRO COMPOUNDS**

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Compound</th>
<th>Colour observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nitrobenzene</td>
<td>D.V.</td>
</tr>
<tr>
<td>2.</td>
<td>p-nitro toluene</td>
<td>D.V.</td>
</tr>
<tr>
<td>3.</td>
<td>m-dinitrobenzene</td>
<td>D.V.</td>
</tr>
<tr>
<td>4.</td>
<td>o-nitro toluene</td>
<td>D.V.</td>
</tr>
<tr>
<td>5.</td>
<td>o-nitro-p-toluidine</td>
<td>D.V.</td>
</tr>
<tr>
<td>6.</td>
<td>o-nitro aniline</td>
<td>D.V.</td>
</tr>
<tr>
<td>7.</td>
<td>p-nitro anisole</td>
<td>D.V.</td>
</tr>
<tr>
<td>8.</td>
<td>o-nitro benzoic acid</td>
<td>D.V.</td>
</tr>
<tr>
<td>9.</td>
<td>m-nitro tolulol</td>
<td>D.V.</td>
</tr>
<tr>
<td>10.</td>
<td>m-nitro benzaldehyde</td>
<td>D.V.</td>
</tr>
<tr>
<td>11.</td>
<td>α-nitro naphthalene</td>
<td>D.V.</td>
</tr>
<tr>
<td>12.</td>
<td>m-nitro aniline</td>
<td>R.B.</td>
</tr>
<tr>
<td>13.</td>
<td>Picric acid</td>
<td>D.G. Bl. on</td>
</tr>
</tbody>
</table>

adding Zn dust and NH₄Cl no change further
TABLE 30 (Contd.)

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Compound</th>
<th>Colour observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.</td>
<td>p-nitro phenol</td>
<td>D.V.</td>
</tr>
<tr>
<td>15.</td>
<td>p-nitro-benzene-azo chromotropic acid</td>
<td>P.V. in alcohol</td>
</tr>
<tr>
<td>16.</td>
<td>p-nitro aniline</td>
<td>D.V.</td>
</tr>
<tr>
<td>17.</td>
<td>P-P'-dinitrodiphenyl carbazide</td>
<td>D.B.</td>
</tr>
<tr>
<td>18.</td>
<td>Hexa-nitro diphenyl amine</td>
<td>P. colour</td>
</tr>
</tbody>
</table>

Abbreviations:
- D.V. = Deep violet
- P.V. = Pinkish violet
- D.G.Bl. = Dark greenish blue
- R.B. = Reddish-brown
- D.B. = Dark-brown

Optimum wavelength: The violet colour obtained with nitro benzene in the manner described above has the spectrum given in Figure 23. The optimum wavelength is 550 nm. The optimum wavelengths of the other compounds are 540 nm, 545 nm, 545 nm and 540 nm for m-nitro benzaldehyde, p-nitro phenol, p-nitro toluene and p-nitroaniline respectively. In all these 5 cases the colour was violet and $\lambda_{max}$ was nearly 550 nm.

Effect of ferric nitrate: Using nitrobenzene as test compound. The complex formation depends upon the amount of ferric nitrate added. Increasing the amount of ferric nitrate increases the absorbance up to 0.8 ml of Fe(NO₃)₃. Addition of more ferric nitrate results in
Fig. 23  Spectrum of violet complex from Nitrobenzene.
decreasing the absorbance. Therefore 0.8 ml \( \text{Fe(NO}_3\text{)}_3 \) is recommended.

**Effect of acetyl chloride:** The complex formation depends much on the amount of acetyl chloride. Increasing the amount of acetyl chloride decreases the absorbance the best result was obtained using 0.08 ml of acetyl chloride for nitrobenzene.

**Effect of time:** The time of shaking after addition of zinc dust and \( \text{NH}_4\text{Cl} \) was 5 minutes. The formation of coloured complex takes 5 minutes and the absorbance remains unchange for 2 hours. A slight decrease in absorbance was recorded after 24 hours.

**Effect of pH:** To study the effect of pH various buffer solutions were added to the reaction mixture. It was observed that the formation of the complex for nitro compounds (nitrobenzene) depends upon pH. The maximum absorbance for nitrobenzene was obtained at pH 0.5 and on addition of buffers of pH higher than 1, precipitation occurs.

**Interferences:** Certain organic compounds were added to nitrobenzene and it was found that chlorobenzene, bromobenzene, iodobenzene, acetic anhydride and acetic acid have no effect, whereas aniline, benzaldehyde and acetone interfere.

**Composition of the complex:** The composition of the complex obtained from nitrobenzene was studied by Job's method of continuous variation and the result is shown in figure 24.

**Calibration graphs:** Calibration graphs were prepared by using 0.8 ml of \( \text{Fe(NO}_3\text{)}_3 \) solution and the procedure described above for 50 \( \mu \text{g} \) to 10 mg of respective nitro compounds. The results are shown in Figure 25.
Fig. 24. Plot of continuous variation method for the violet coloured complex.
DISCUSSION

(Figure 25) shows that aromatic nitro compounds can be determined spectrophotometrically using the proposed procedure. The Beer's law is obeyed in the range of 50 \( \mu \text{g} \) to 10 mg for nitrobenzene, \( p \)-nitro aniline, \( m \)-nitrobenzaldehyde, \( p \)-nitro toluene and \( p \)-nitro phenol. The sequence of the reactions can be represented as follows:

\[
\begin{align*}
\text{ArNO}_2 + 2\text{Zn} + \text{H}_2\text{O} & \rightleftharpoons \text{ArNHOH} + 2\text{ZnO} \\
\text{ArNHOH} + \text{CH}_3\text{COCl} & \rightleftharpoons \text{CH}_3\text{CO NOHAr} + \text{HCl} \\
3\text{CH}_3\text{CO NOHAr} + \text{Fe}^{3+} & \rightleftharpoons \left[\text{Fe}^+ (\text{CH}_3\text{CONOAr})_3\right] + 3\text{H} + \text{coloured complex}
\end{align*}
\]

The formation of Ar NHOH takes place at a pH-5.5 using \( \text{NH}_4 \text{Cl} \) and zinc dust while the formation of coloured complex with \( \text{Fe}^{3+} \) after adding \( \text{CH}_3\text{COCl} \) takes place at a lower pH 0.5. The initial pH 5.5 decreases to pH 0.5 by the addition of acidified ferric nitrate. A similar mechanism is given by Davidson (5) using benzoyl chloride. He has used hydrochloric acid to make the solution acidic.

The formation of violet coloured complex depends upon the concentration of acetyl chloride, ferric nitrate, pH. The results
op pH effect show that pH = 0.5 is optimum for the measurement of aromatic nitro compounds (only nitrobenzene tested). It is clear from (Figure 24) that the complex forms in the ratio of \( \text{RN}_{2} : \text{Fe}^{3+} \) (2:3). The stability (7) of the complex is quite high (\( K = 10.7 \times 10^3 \) for nitrobenzene). The results show that coloured complex formed is stable for 2 hours very little change in absorbance is observed in 24 hours for all the five compounds tested. However, it takes 5 minutes for the development of the colour.
LITERATURE CITED


