CHAPTER VII

SPECTROPHOTOMETRIC DETERMINATION OF p-NITROANILINE USING N(1-NAPHTHYL)ETHYLENE DIAMINE DIHYDROCHLORIDE

SUMMARY

The method describes the determination of p-nitroaniline in which p-nitroaniline is diazotised with sodium nitrite in the presence of hydrochloric acid and subsequently coupled with N(1-Naphthyl)-ethylene diamine dihydrochloride in acidic medium. The absorbance of the purple coloured dye so formed is measured at 545 nm. The molar absorptivity and Sandell's sensitivity were found to be $6.6 \times 10^4$ lit. mol$^{-1}$cm$^{-1}$ and 0.0021 $\mu$g cm$^{-2}$ respectively. Several common interferents like phenols, nitro compounds, aldehydes present in polluted water do not interfere.

SPECTROPHOTOMETRIC DETERMINATION OF p-NITROANILINE USING N(1-NAPHTHYL)ETHYLENEDIAMINE DIHYDROCHLORIDE

p-Nitroaniline (PNA) is widely used in the synthesis of diesters and as intermediate in the synthesis of 'aniline' dyes, accelerators and antioxidants for rubber industry. Several amines are classed as 'fur' dyes although they actually are not dyestuffs because they have no tinctorial value in their unoxidised form. Nitro and amino derivatives find great importance in commercial use. These compounds are used in the production of paints, varnishes, shoe polishes, fungicides, plastics, petroleum products and synthetic resins (1). It is highly toxic and a susceptible carcinogen in the presence of sodium nitrite (2). p-Nitroaniline has a strong ability to form methemoglobin in man, with attendant homolytic effect (3). The only safe and reliable index is a qualitative determination of methemoglobin content of venous blood by an accepted method (1). p-Nitroaniline is fat soluble and is readily absorbed through the intact skin and its vapours are toxic as well. Threshold Limit Value as established by American Conference of Governmental Industrial Hygienists is 1 ppm (1).
Literature survey shows that very few methods have been reported for the detection and determination of p-nitroaniline (4-8). The methods are either based on oxidative coupling (9-11) or diazotisation reaction and their subsequent coupling (12-14). But these methods mostly lack selectivity due to the interference of other primary aromatic amines. The final product formed by both the above mentioned reactions with other amines too have the same wavelengths of maximum absorption. Other methods though selective, lack sensitivity. In the proposed method for the quantitative determination of p-nitroaniline, the well known diazotisation coupling reaction is made use of (15). p-Nitroaniline is diazotised in hydrochloric acid medium and is subsequently coupled with M(1-naphthyl)ethylene diamine dihydrochloride (NEDA). The purple coloured dye so formed has an absorption maxima at 545 nm. The optimum reaction conditions and other analytical parameters have been investigated.

**EXPERIMENTAL**

**Apparatus:** An ECIL spectrophotometer model GS-865 and Carl Zeiss Spekol with 1 cm matched silica cells were used for all spectral measurements.

**Reagents:**

**Standard p-nitroaniline solution:** A stock solution of 0.1% (w/v) p-nitroaniline was prepared in
excess of nitrite. After this 2.5 ml of NEDA solution was added and the volume made up to the mark with 6 M hydrochloric acid. This was kept for 15 minutes for full colour development. The purple coloured dye so formed was measured at 545 nm using distilled water as reference.

Method for Solvent Extraction:

An aliquot (~100 ml) of water sample containing 10-40 μg (0.1 to 0.4 ppm) of p-nitroaniline was transferred into a 250 ml separatory funnel. 0.5 ml nitrite solution was added and the acidity was adjusted to ~0.5 M with hydrochloric acid and the solution was allowed to stand for 2-3 minutes. Then 2.5 ml of sulphamic acid and 2.5 ml NEDA solution were added. The purple dye formed was extracted with 15 and 10 ml aliquots of iso-amyl alcohol. The extract was dried over anhydrous sodium sulphate and the absorbance measured at 545 nm. A reagent blank extracted in iso-amyl alcohol was used as reference for absorbance measurements.

RESULTS AND DISCUSSIONS

Absorption spectra:

Absorption spectra of the azo dye in aqueous and extractive system shows a wavelength of maximum absorption at 545 nm (Fig. 1). Absorption of the reagent blanks were negligible in this region.
20% aqueous ethanol. A working standard containing 10 µg/ml p-nitroaniline was prepared by appropriate dilution of the stock with demineralised water. The commercially available reagent was crystallised twice before use.

Standard nitrite solution: A stock solution of 1 mg/ml of sodium nitrite was prepared in demineralised water. Working standard of 200 µg/ml was prepared by appropriate dilution of the stock.

N(1-naphthyl)ethylene diamine dihydrochloride (NEDA) solution: 0.2% (w/v) solution of NEDA was prepared in demineralised water.

Sulphamic acid solution: 0.6% (w/v) solution of sulphamic acid was prepared in demineralised water.

Solution of Diverse Ions: These were prepared by the method of West (16).

All Chemicals used were of AnalaR grade.

Procedure:

An aliquot of the sample containing 10-40 µg of p-nitroaniline (0.4 to 1.6 ppm) was taken in a 25 ml volumetric flask. To this was added 0.5 ml of sodium nitrite solution followed by the addition of 0.2 ml of concentrated hydrochloric acid to adjust the acidity to ~0.5 M and then the solution was allowed to stand for 2-3 minutes for complete diazotisation. Then 2.5 ml of sulphamic acid solution was added to destroy the
FIG. 1. ABSORPTION SPECTRA OF THE DYE.

A. CONCENTRATION OF PNA - 20μg/25ml.

B. CONCENTRATION OF PNA - 30μg/100ml.
(EXTRACTIVE SYSTEM)
Effect of Variables:

The effect of acidity on the diazotisation and coupling were studied. Results show that, at least 0.02 M hydrochloric acid was necessary for complete diazotisation and constant absorbance values were obtained over the acidity range of 0.02 to 3.0 M hydrochloric acid (Fig. 2).

The necessary time for complete diazotisation was determined. The absorbance values were found constant for a period of 90 minutes. The diazotisation was fast at ~30°C and constant results were obtained between 10° to 40°C.

Effect of varying molar ratios of p-nitroaniline and nitrite were examined. At least 1:1 mole ratio of p-nitroaniline and nitrite was necessary for full colour development and upto 20 fold molar excess, constant values were obtained (Fig. 3). Similarly, the maximum absorbance was obtained at a NO₂ : NEDA ratio of 1 : 10 and higher concentration of NEDA did not effect absorbance values (Fig. 4).

Beer's Law, Molar absorptivity, Sandell's sensitivity and Reproducibility:

The colour system was found to obey Beer's law in the range of 10 to 40 μg of p-nitroaniline per 25 ml (Fig. 5) (0.4 to 1.6 ppm) of the aqueous system whereas for the extractive system, it was 10 to 40 μg per 100 ml of the sample (0.1 to 0.4 ppm).
**FIG. 2. EFFECT OF ACIDITY ON DIAZOTIZATION REACTION**

CONCENTRATION OF HYDROCHLORIC ACID - M

**CONCENTRATION OF PNA - 20μg/25ml.**

**FIG. 3. EFFECT OF AMOUNT OF NITRITE ON COLOUR REACTION.**

CONCENTRATION OF PNA - 20μg/25ml.
FIG. 4. EFFECT OF NEDA ON COLOUR REACTION AMOUNT OF PNA = 20μg/25ml.

FIG. 5. CALIBRATION CURVE FOR p-NITROANILINE WITH NITRITE AND NEDA.
The molar absorptivity and Sandell's sensitivity for aqueous and extractive systems were found to be $6.6 \times 10^4 \text{ lit. mol}^{-1}\text{cm}^{-1}$ and 0.0021 $\mu\text{g cm}^{-2}$ respectively.

Reproducibility of the method was checked by seven replicate analyses (Table I) by taking 20 $\mu\text{g}$ of p-nitroaniline over a period of seven days. The data in Table I were employed to compute standard deviation and relative standard deviation which were found to be $\pm 0.007$ and 1.86% respectively.

**Effect of Diverse Species:**

The effect of diverse species was studied by adding known amounts of diverse species commonly present in polluted water, and determining p-nitroaniline as recommended in the procedure. Tolerance limit shown in Table II are the amounts of foreign ions that cause a $\pm 2\%$ error in the determination of the proposed amount of p-nitroaniline.

**Effect of Solvent Extraction:**

Solvent extraction using different organic solvents were employed to increase the sensitivity of the reaction. Iso-amyl alcohol was found to be the most suitable of the various solvents tried. The dye was found to be unstable in chloroform and complete extraction of the dye did not take place in benzene, dichlorobenzene, carbon tetrachloride. In higher alcohols like hexanol and octanol the extraction was
TABLE - I

REPRODUCIBILITY OF THE METHOD

Concentration of p-nitroaniline = 0.8 ppm

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance $\lambda_{\text{max}}$ = 545 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.380</td>
</tr>
<tr>
<td>2</td>
<td>0.375</td>
</tr>
<tr>
<td>3</td>
<td>0.380</td>
</tr>
<tr>
<td>4</td>
<td>0.370</td>
</tr>
<tr>
<td>5</td>
<td>0.385</td>
</tr>
<tr>
<td>6</td>
<td>0.370</td>
</tr>
<tr>
<td>7</td>
<td>0.365</td>
</tr>
</tbody>
</table>

Mean = 0.375

Standard deviation = $\pm$ 0.007

Relative standard deviation = 1.86%
## TABLE - II

**EFFECT OF DIVERSE IONS**

Concentration of p-nitroaniline = 0.8 ppm

<table>
<thead>
<tr>
<th>Diverse Ion</th>
<th>Tolerance limit in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{3+}$ (25)$^a$, $\text{Cr}^{6+}$ (10), $\text{Co}^{3+}$ (100),</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+}$ (100), $\text{Zn}^{2+}$ (100), $\text{Cd}^{2+}$ (100),</td>
<td></td>
</tr>
<tr>
<td>$\text{Hg}^{2+}$ (100), $\text{Be}^{2+}$ (100), $\text{Sb}^{3+}$ (100),</td>
<td></td>
</tr>
<tr>
<td>$\text{Se}^{4+}$ (100), $\text{Mg}^{2+}$ (150), $\text{Ca}^{2+}$ (150),</td>
<td></td>
</tr>
<tr>
<td>$\text{Sr}^{2+}$ (150), $\text{Ba}^{2+}$ (150)$^b$, $\text{Pb}^{2+}$ (150)$^b$,</td>
<td></td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$ (20), $\text{I}^-$ (40)$^c$, Phenol (40),</td>
<td></td>
</tr>
<tr>
<td>Chlorophenol (40), Formaldehyde (40),</td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene (50), Benzene (500),</td>
<td></td>
</tr>
<tr>
<td>Aniline (20), Methanol (400),</td>
<td></td>
</tr>
<tr>
<td>Acetone (400), Pyridine (250),</td>
<td></td>
</tr>
<tr>
<td>Chloroform (500)</td>
<td></td>
</tr>
</tbody>
</table>

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$a$ - Masked with 1 ml 10% sodium potassium tartarate.

$b$ - Masked with 1 ml 10% hydrogen peroxide solution.

$c$ - Masked with 1 ml TCM solution.
complete but molar absorptivity decreased. Thus by extraction in iso-amyl alcohol submicrogram quantities i.e. 0.1 ppm of p-nitroaniline could be determined in a large volume of sample ~100 ml.

CONCLUSION

The reported method is rapid, reproducible, sensitive and free from the interferences of large group of diverse species. Solvent extraction enables to determine very low amount of p-nitroaniline in large volume of samples.
REFERENCES


