Chapter - 2
SPECTROPHOTOMETRIC DETERMINATION OF NITROGEN DIOXIDE IN THE ENVIRONMENT

Summary

In the present investigation a simple, sensitive and selective spectrophotometric method for the determination of nitrogen dioxide in air has been described. The air sample containing nitrogen dioxide is passed through the absorbing solution of acidified potassium iodide to liberate iodine. The liberated iodine reacts with leucocrystal violet (LCV) to form crystal violet dye, which is measured at 590 nm. The proposed reagent has ~ 99% collection efficiency and stoichiometric ratio of 0.74 for NO$_2$: NO$_2$. Beer’s law is obeyed over the concentration range of 0.1-1.0 µg of nitrite per 25 ml of the final solution (0.004-0.04 ppm). The molar absorptivity and Sandell’s sensitivity were found to be $1.5 \times 10^6$ 1 mol$^{-1}$ cm$^{-1}$ and $4.4 \times 10^5$ µg cm$^{-2}$ respectively. Other analytical parameters have been optimized. The method has been applied for the determination of nitrogen dioxide in laboratory air, auto exhaust and cigarette smoke.

INTRODUCTION

Nitrogen dioxide (NO₂) is an important atmospheric trace gas, not only because of its health effects but also because it absorbs visible solar radiation and contributes to impaired atmospheric visibility; has a potential direct role in global climate change if its concentrations become high enough; regulates the oxidizing capacity of the free troposphere by controlling the build-up and fate of radical species and plays a critical role in determining ozone concentrations in the troposphere because the photolysis of nitrogen dioxide is the only key initiator of the photochemical formation of ozone (1-3). Nitrogen dioxide is one of the most hazardous primary air pollutants and is one of the six criteria air pollutants for which National Ambient Air Quality Standards are set by US Environmental Protection Agency (4-6). The natural sources include intrusion of stratospheric nitrogen oxides, bacterial and volcanic action and lightning. The primary anthropogenic sources of outdoor nitrogen dioxide are vehicles, burning of solid wastes, brick kiln, fossil fuel burning power plants and industrial boilers. In most ambient situations, nitric oxide is emitted and transformed into nitrogen dioxide in the atmosphere (7-10). Other sources of nitrogen dioxide in the atmosphere are non-combustion industrial processes, such as the manufacture of nitric acid, the use of explosives, electroplating, engraving and welding (11). Indoor sources include cigarette smoking and the use of gas stoves, gas hot water heaters, gas and kerosene space heaters, oil stoves, poorly vented furnaces and fire places (12-15). NO₂ also plays an important role in photochemical smog production (16-17).

Exposure to indoor nitrogen dioxide (NO₂) is of public health concern since indoor concentration is reported to be higher than outdoor concentration and a seasonal variation with higher levels in winter has also been reported (14-15,18). Indoor sources tend to be the dominant contributors to personal exposure in urban areas, due to the large percentage of time spent inside their homes. This is especially true for extremely young children, the elderly, and the ill (19-21). In addition to indoor sources, automobile traffic has been recognized as a major source of exposure (22-23). In the environment, nitrogen dioxide exists as a gas and the relevant route
of exposure to humans is inhalation. Studies have shown that even low level of exposure to NO₂ increased bronchial reactivity in some asthmatics, decreased lung function in patients with chronic obstructive pulmonary disease and increased risk of respiratory infection in young children (24-27). The effects of short term exposure include irritation to eyes and nasal passages, throat, lower respiratory passages, shortness of breath, cough, cold, wheezing, narrowing of bronchi, and accumulation of fluid in lung, cardiac dilation and methemoglobinemia (18, 28-29). Nitrogen dioxide induces methemoglobinemia by nitrite oxidation of haemoglobin from the ferrous to the ferric form. The ferric form of haemoglobin does not reversibly bind oxygen and death results from it in reverse cases as pointed out by Von Oettingen (30-31). It may combine with secondary, tertiary amines and amides in the stomach to form highly carcinogenic nitrosamines (32-33). High concentration exposure causes burns, spasms, swelling of tissues in throat, upper airway obstruction and death; irritation, clouding of eye surface and blindness and chronic exposure can contribute to bronchitis, asthma and bronchiolar damage. The permissible exposure limit value (PEL) and OSHA STEL for nitrogen dioxide are 5 ppm and 1 ppm, respectively for 15 min exposure. The NIOSH IDLH is 50 ppm (34-35).

The significance of nitrogen dioxide as a toxic ubiquitous pollutant has culminated in the development of several analytical sampling techniques and methods for its determination and detection. These include chemiluminescence (36-37), photoacoustic spectroscopy (38), laser photo fragmentation (39), tunable laser (40), laser induced fluorescence (41), gas chromatography (42-43), liquid chromatography (45), ion chromatography (46-48), amperometric (49-50), fluorimetry (51), thermal lens spectrophotometry (52), electrochemical (53), sensors (540, ozone scrubber (55) etc. Few methods using solid sorbent systems (48), chromatomembrane cell (56-57), carbon coated annular diffusion denuder (58), Palmses tubes, filters mounted in diffusion badges (59), fibre optic spectroscopy (60), piczo-dosimeter (61) and passive sampling devices (62-63) have also been reported.

A large number of spectrophotometric methods (64-72) have been reported in the literature for the determination and detection of nitrogen dioxide. Most of the
spectroscopic methods are based on Greiss reaction (64) using regents such as p-nitroaniline – guaiacol (65), 8-hydroxyquinolene (66), 1-aminonaphthalene-2-sulphonic acid (67), N-(1-naphthyl) ethylene diamine (NEDA), p-aminoacetophenone and oxalic acid (68), p-nitroaniline – chromotropic acid (69), sulfathiazole-NEDA (70) have also been reported.

Here a simple and sensitive method using a chromogenic reagent leucocrystal violet has been reported. The proposed method is based on the liberation of iodine by the reaction between absorbing solution (KI + HCl) and nitrogen dioxide present in air. The liberated iodine selectively oxidises LCV to form crystal violet having absorption maxima at 590 nm. The proposed reagent has ~ 99 % collection efficiency and the stoichiometric ratio of NO₂: NO₂⁻ is 0.74, which is in agreement with the values reported in literature (73).

**EXPERIMENTAL**

**Apparatus**

A Systronics 106 digital spectrophotometer and a Systronics 335 pH meter were used for spectral and pH measurements. For air sampling midget impingers of 35 ml capacity were used and flow rate was controlled by rotameter.

**Reagents**

All chemicals used were of analytical reagent grade or the best quality available and double distilled water was used throughout the experiment.

**Standard sodium nitrite solution [MERCK]:** A stock solution of sodium nitrite containing 1mg ml⁻³ of nitrite was prepared by dissolving 0.150 g of predried sodium nitrite in 100 ml of distilled water. A small amount of chloroform was added as a stabilizer (74). Working standard solution was prepared daily by dilution of stock.

**Potassium iodide [MERCK]:** 1% aqueous solution
Leuco crystal violet (LCV) [EASTMAN KODAK CO.]: In a 100 ml volumetric flask containing 20 ml of water, 0.3 ml of 85% phosphoric acid, 25 mg of LCV was added and shaken gently until the dye dissolved. The content of the flask was then diluted to 100 ml with water. This solution was stable for long period when kept in amber coloured bottle.

*Hydrochloric acid: 6 M solution was used.*

*Absorbing solution:* The absorbing solution was prepared by mixing 7 ml of potassium iodide and 1 ml of HCl solution and diluted to 10 ml with distilled water.

*Sodium Hydroxide [LOBA CHEMIE]:* 1 M aqueous solution

*Procedure*

Nitrogen dioxide was prepared by bubbling purified air through fresh nitrite solution as described by Nash (75). An aliquot of a solution containing 0.1 to 1.0 µg of nitrite was taken in an impinger kept in a hot water bath ~ 60°C to which 5 ml of 6 M hydrochloric acid was added dropwise from a micro burette to liberate nitrogen dioxide. The liberated nitrogen dioxide was absorbed in the absorbing solution taken in two midget impingers of 35 ml capacity each containing 10 ml of absorbing solution connected to source of suction. The air was passed through the solution at a rate of 0.5 l min⁻¹ for 15 min and the contents of the two impingers were mixed in a 25 ml graduated tube. To this 1 ml of LCV was added and the pH of solution was adjusted to pH 4.0-4.5 with ~ 3-4 drops of 1 M sodium hydroxide. The content was diluted up to the mark with water and kept in a water bath at 40-45°C for 2-3 min. The solution was left for 20-25 min at room temperature for complete colour development and the absorbance was measured at 590 nm against reagent blank.
RESULTS AND DISCUSSION

Spectral characteristics
The absorption spectra of the crystal violet dye showed a maximum absorbance at 590 nm against reagent blank and the reaction is represented in Scheme 1. The reagent blank showed negligible absorbance at this wavelength (Fig. 1).

Adherence to Beer’s law, molar absorptivity and Sandell’s sensitivity
The colour system obeys Beer’s law over the range 0.1 - 1.0 μg of nitrite per 25 ml (0.004-0.04 ppm) (Fig. 2). The molar absorptivity and Sandell’s sensitivity as calculated from the slope were found to be $1.5 \times 10^6$ l mol$^{-1}$ cm$^{-1}$ and $4.4 \times 10^{-5}$ μg cm$^{-2}$ were found to be respectively.

Collection efficiency
The collection efficiency was determined by passing air containing nitrogen dioxide through two midget impingers connected in series, each containing 10 ml of absorbing solution at a flow rate of 0.5 l min$^{-1}$ for 15 min. The results show that the proposed reagent has ~ 99% collection efficiency in the first impinger. The effect of flow rate on the collection efficiency was also studied. It was observed that collection efficiency of the first impinger decreases with the increase of flow rate (Table 1).

NO$_2$: NO$_2^-$ Stoichiometric factor
The colour produced by absorbing a given amount of nitrogen dioxide can also be compared with that produced by adding equimolar amount of nitrite. The ratio of their absorbance values is known as stoichiometric factor or sometimes referred as Saltzman factor. There are differences in the reported values for the stoichiometric factor. According to Saltzman it is 0.72 while Startman and Buck and Huygen reported it to be nearly unity. The NO$_2$: NO$_2^-$ stoichiometric factor (76) for the
proposed method has been evaluated and found to be 0.74, which is in agreement with values in the literature.

Effect of reagent concentration
Under the proposed reaction conditions, it was observed that for absorbing solution, 7 ml of 1% potassium iodide (Fig. 3) and 1 ml of 6 M HCl solution diluted to 10 ml with distilled water was necessary for maximum absorption. It was found that 1 ml of LCV (Fig. 3) and 3-4 drops of 1 M sodium hydroxide solution were sufficient for maximum colour development.

Effect of time and temperature
Under optimum condition, 40-45°C was found to be the most suitable temperature since above and below this range absorbance was markedly affected. It was found that 25 min time was essential for complete colour development and the colour was stable for several days (Fig. 4).

Effect of pH
The most suitable range of pH was found to be 4.0 - 4.5 for the formation of crystal violet from LCV. The pH was maintained by using 1 M sodium hydroxide. Higher pH severely affected the stability of the dye and at lower pH colour development did not take place.

Reproducibility
Reproducibility of the method was checked by seven replicate analysis of the solution containing 1.0 µg of nitrite per 25 ml final solution. The standard deviation and relative standard deviation were found to be ± 0.0097 and 2.16% respectively.

Effect of diverse ions
The effect of diverse ions commonly found with nitrogen dioxide was studied by adding known amount of diverse ions into the absorbing solution before sampling. Interferences from sulphur dioxide and heavy metals were masked with 1 ml of 1%
hydrogen peroxide and EDTA respectively. Carbon monoxide, carbon dioxide, ammonia, formaldehyde and phenol, which are present in air with nitrogen dioxide, have no effect on colour development.

**COLOUR REACTION**

The colour reaction involves the following steps (Scheme 1):

- Nitrogen dioxide reacts with acidified potassium iodide to produce iodine.
- The liberated iodine oxidizes LCV to crystal violet dye.

**APPLICATION**

1. Determination of nitrogen dioxide in air

The proposed method was applied for the determination of nitrogen dioxide in polluted air. Burning 1 g of coal powder liberated the nitrogen dioxide. An air sampling train was fitted in the laboratory and the air containing nitrogen dioxide was passed at the rate of 0.5 l min\(^{-1}\) for 10 min through two midget impingers, each containing 10 ml of absorbing solution, connected to a source of suction. The absorbing solutions were mixed and suitable aliquots were then analysed by the present and reported method (67) (Table 2).

2. Determination of nitrogen dioxide in cigarette smoke

Smoke from various brands of cigarettes with and without filter was drawn through three midget impingers connected to air sampling train. The first two containing acidic potassium permanganate (2.5% KMnO\(_4\), w/v in 2.5% H\(_2\)SO\(_4\)) for oxidation of nitric oxide to nitrogen dioxide and the third impinger containing 10 ml of the absorbing solution (77). The cigarette was marked at the required butt length. The lighted cigarette was fixed in the glass holder and the air was sucked at the rate of 0.25 l min\(^{-1}\) till the marked length. After sampling the aliquots were analyzed by the present and reported method (67) (Table 2).
3. Determination of nitrogen dioxide auto exhaust

Nitrogen dioxide present in auto exhaust was drawn through the two midget impingers each containing 10 ml absorbing solution and attached to an air sampling train. After sampling the absorbing solution were mixed and aliquots were then analysed by the present and reported method (67) (Table 2).

CONCLUSION

The present method for the determination of nitrogen dioxide is simple sensitive and avoids the use of hazardous chemicals. This method can be compared favorably with the reported methods (Table 3). The method can be successfully applied to the trace determination of nitrogen dioxide in polluted air.
1. \( \text{NO}_2 + 2 \text{I}^- \xrightarrow{\text{H}^+} \text{I}_2 \)
   Nitrogen dioxide  Iodide  Iodine

2. \( \text{I}_2 \xrightarrow{} \)
   Iodine

   \[
   \begin{array}{c}
   \text{N}(\text{CH}_3)_2 \\
   \text{C} \\
   \text{N}(\text{CH}_3)_2 \\
   \text{CH} \\
   \text{N}(\text{CH}_3)_2 \end{array}
   \]
   \[
   \begin{array}{c}
   \text{N}(\text{CH}_3)_2 \\
   \text{C} \\
   \text{N}(\text{CH}_3)_2 \\
   \text{CH} \\
   \text{N}(\text{CH}_3)_2 \end{array}
   \]
   Leucocrystal Violet  Crystal Violet
   \( \lambda_{\text{max}}: 590 \text{ nm} \)

Scheme 1: Colour Reaction of Nitrogen Dioxide
### Table 1. Effect of flow rate on absorption efficiency
(Sampling time ~ 15 min)

<table>
<thead>
<tr>
<th>Flow rate (L min⁻¹)</th>
<th>Total amount of NO₂ (µg)</th>
<th>NO₂ absorbed in first impinger (µg)</th>
<th>Collection efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.500</td>
<td>0.495</td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>0.990</td>
<td>99.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.500</td>
<td>0.498</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>0.994</td>
<td>99.4</td>
</tr>
<tr>
<td>1.00</td>
<td>0.500</td>
<td>0.491</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>0.980</td>
<td>98.0</td>
</tr>
</tbody>
</table>

### Table 2. Determination of nitrogen dioxide in various samples

<table>
<thead>
<tr>
<th>Source of sample</th>
<th>Nitrogen dioxide found* (ppm)</th>
<th>Present method</th>
<th>Reported method (67)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laboratory air*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.67</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.89</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.93</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>Cigarette smoke*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(with filter)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.41</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.37</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.53</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Cigarette smoke*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(without filter)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.49</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.67</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.79</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Auto exhaust*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.39</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.36</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.43</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>

*Mean of three replicate analyses

a: Volume of air sample -5 litres and b: Smoke per one cigarette
Table 3. Comparison with other spectrophotometric methods

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reagents</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Linear range (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sulphanilic acid + naphthylamine (64)</td>
<td>520</td>
<td>0.05-1.2</td>
<td>$\text{Cu}^{2+}$, $\text{Fe}^{3+}$ and strong oxidants interfere.</td>
</tr>
<tr>
<td>2.</td>
<td>PNA + guaiacol (65)</td>
<td>505</td>
<td>0.03-0.15</td>
<td>Extractive $\text{SO}_3^2$, $\text{NO}_3^-$ are interfere.</td>
</tr>
<tr>
<td>3.</td>
<td>8-hydroxy quinoline + PNA (66)</td>
<td>570</td>
<td>0.07-0.49</td>
<td>Extractive, $\text{Cu}^{2+}$, $\text{Fe}^{3+}$ are interfere.</td>
</tr>
<tr>
<td>4.</td>
<td>o-nitroaniline + 1-amino-naphthalene-2-sulphonic acid (67)</td>
<td>545</td>
<td>0.08-0.64</td>
<td>Extractive, less sensitive</td>
</tr>
<tr>
<td>5.</td>
<td>P - aminoactophenone + NEDA + Oxalic acid (68)</td>
<td>548</td>
<td>0.12-0.96</td>
<td>Heavy metals and $\text{SO}_2$ are interfering.</td>
</tr>
<tr>
<td>6.</td>
<td>PNA + chromotropic acid (69)</td>
<td>515</td>
<td>0.0-0.4</td>
<td>Less sensitive, $\text{HCHO}$ interferes.</td>
</tr>
<tr>
<td>7.</td>
<td>Sulfathiazole-NEDA (70)</td>
<td>546</td>
<td>0.054-0.816</td>
<td>Less sensitive, heavy metals interfere.</td>
</tr>
<tr>
<td>8.</td>
<td>Neutral red (72)</td>
<td>530</td>
<td>0-0.06</td>
<td>Extractive</td>
</tr>
<tr>
<td>9.</td>
<td>Potassium iodide + HCl + LCV (present method)</td>
<td>590</td>
<td>0.004-0.04</td>
<td>Simple, more sensitive, no interference of $\text{Cu}^{2+}$, $\text{Fe}^{3+}$ and heavy metals.</td>
</tr>
</tbody>
</table>
FIG 1. ABSORPTION SPECTRA OF THE DYE AND REAGENT BLANK

A: CONCENTRATION OF NITROGEN DIOXIDE, 0.5 μg / 25 ml
B: REAGENT BLANK

FIG 2. CALIBRATION CURVE FOR THE DETERMINATION OF NITROGEN DIOXIDE
Fig 3. EFFECT OF REAGENT CONCENTRATION ON COLOUR REACTION

Fig 4. EFFECT OF TEMPERATURE AND TIME ON COLOUR REACTION
REFERENCES


