CHAPTER III

MATERIAL AND METHODOLOGY
CHAPTER III: MATERIAL AND METHODS

In this chapter, materials and methods used in this field are described in details, including the site selection and description, chemicals, glassware, instrument and procedures employed for sampling site selection, sampling of air, analysis of pollutant concentration and calculations.

3.1 SITE DESCRIPTION

Air Quality Monitoring Sites:

Sampling locations are in general governed by factors like objectives, method of sampling and resources available. Granting to the objective of my study locations were held close to the objects where the effects are being analyzed and kept at breathing level in the population centers, hospitals, schools, etc. For background concentration, sampling location should be away from the origins of contamination. It can as well be done by gridding the entire country to get statistically recommended values.

a) To gather preliminary information about the study area and principal sources of pollution.

b) To review the available climatological and meteorological data.

c) To gather data on the concentration of pollutants in areas of severe and slight pollution.

During ambient air sampling, it was necessary to collect information on qualitative and quantitative data on the local sources of air pollution, topography, population
distribution, land use pattern etc., depending upon the objectives of the survey or measurement campaign. For example, an area map to locate pollution sources and monitoring locations, sources of pollution situated at far distances, etc. and other relevant data that describe the behavior of the atmosphere for a specific pollutant to be sampled may also be required. Site selection must consider the location of identified or suspected sensitive receptors and the locations where the highest concentrations of air contaminants are anticipated based on meteorological and modeling information. Monthly, quarterly and half yearly wind roses were constructed from the wind data, i.e. its speed and direction, collected for the period of 12 months i.e. January 2011 to December 2013 by using weather monitoring institutes. The site for installation of weather monitoring station was an open area with no obstruction to ensure accurate measurement of wind speed and direction. So for this study, three sites were selected as,

1. S1-I-VIP (19°59'54.64"N, 73°43'41.18"E) - Industrial site, Nashik.
2. S2-R-RTO (19°59'49.10"N, 73°46'35.25"E) - Residential site, Nashik.
3. S3-C-NMC (20°00'10.17"N, 73°47'21.55"E) - Commercial site, Nashik.

In the wind rose, each concentric circle represents a different frequency, emanating from zero at the center to increasing frequencies at the outer circles. Using a polar coordinate system of grading, the frequency of winds over a long time period were plotted by wind direction, with color bands showing wind ranges. In order to plot wind rose diagram, seven different wind speed ranges were taken into consideration. The direction of the wind rose with the longest spoke shows the wind direction with
maximum frequency. Calm period was taken for speed range <1kph and it was included in the center of the diagram. After plotting wind roses, the impact area diagram was constructed using methodology given in George et al., 2009. Impact area diagrams were drawn by superimposing all the sector area over one center having an arc radius equal to the average wind speed (George et al., 2008). Impact area diagrams are helpful in obtaining the idea about the most affected wind direction from the source. Wind data were then grouped into different categories of wind speed, and for each wind speed category, the average distance traveled by the pollutant per unit time from the source were being represented by the mean wind speed (V_j) of that category. For example, wind speed category can be taken from 1 to 3, 3 to 5, 5 to 7 and 7 to 9 kmh⁻¹ etc. For calculating standard deviation, wind speeds more than 1 kmh⁻¹ were taken into consideration excluding calm wind conditions. Impact area under different wind speed categories were summed up to obtain the total impact area (George et al., 2009). Since different wind speed groups may indicate different direction of the impact area, its linear summation was weighted by the persistence of the impact area, thereby yielding dilution potential. The standard deviation (σ₀) of the wind direction is estimated from Yamartino method (Yamartino, 1984; Isikwue et al., 2010).

\[
s_a = n^{-1} \sum_{i=1}^{n} \sin \Theta_i \quad \text{(1)}
\]

\[
c_a = n^{-1} \sum_{i=1}^{n} \cos \Theta_i \quad \text{(2)}
\]
First of all, average of sine and cosine of wind direction angle was calculated using equation 1 and 2 for each specific wind speed class. Then these average values were used to calculate the average wind direction for that specific wind speed class (Farrugia and Micallef, 2006). Average wind direction was calculated using the four-quadrant arctan \((x, y)\) function as mentioned in equation 3. Values of \(c_a\) and \(s_a\) were taken without any positive and negative sign (Gaile and Burt, 1980).

\[
\Theta = \tan^{-1}\left(\frac{s_a}{c_a}\right) \tag{3}
\]

But values obtained from above equation needs correction as a sign of \(c_a\) and \(s_a\) are neglected in the above formula. So to calculate final average wind directions following condition was used.

\[
\Theta = \begin{cases} 
180 + \Theta & \text{if } s_a < 0 \text{ and } c_a < 0 \\
180 - \Theta & \text{if } s_a > 0 \text{ and } c_a < 0 \\
\Theta & \text{if } s_a > 0 \text{ and } c_a > 0 \\
360 - \Theta & \text{if } s_a < 0 \text{ and } c_a > 0
\end{cases}
\]

Consider an example that if the value obtained for \(\Theta\) is 60° from equation 3, with a value of \(c_a\) with negative and \(s_a\) with positive sign, means the final value of \(\Theta\) will lie in 2\textsuperscript{nd} quadrant. This is due to the fact that in 2\textsuperscript{nd} quadrant, sine function has positive value and cosine function has negative value. Then the final value taken for \(\Theta\) is 120° i.e. by applying 2\textsuperscript{nd} condition by which \(180° - 60° = 120°\) is the final value for \(\Theta\).

For the calculation of standard deviation, first \(\epsilon\) is calculated using the values of \(s_a\) and
$c_a$ using the following equation. This value of $E$ is then used to estimate the value of standard deviation which can be obtained by using equation 4.

$$\sigma_\theta = \left[ \sin^{-1}(E) \right] \left[ 1 + \{(2/\sqrt{3})-1\} \ E^3 \right]$$ \hspace{1cm} (4)

Where,

$$E = [1-(s_a +c_a)]$$

Mean wind speed was calculated by just taking the average of all the value of wind speed obtained within a specific wind speed class. Impact area can be calculated by using equation 5 (George et al., 2009).

$$aj = \frac{\sigma_\theta}{2} \left[ V_j^2 \times n_j / (N-N_{calm}) \right]$$ \hspace{1cm} (5)

Where,

$\sigma_\theta = $ angular standard deviation of the specific group;

$V_j = $ mean wind speed for the specific group;

$n_j = $ number of wind data in specific wind speed category;

$N_{calm} = $ number of wind data in calm period range (<1kph) and

$N = $ total number of wind data.

Values for standard deviation, mean wind direction calculated earlier were used to calculate impact area.
3.2 INSTRUMENTS

3.2.1 High Volume Sampler with gaseous attachment

High Volume Samplers (Fig: 3.2) were the basic instruments used to monitor ambient air quality. In this study, Envirotech APM 415 with its attachment for gaseous pollutant monitoring APM 411 was used (Oline J.G. et al., 1975)
In these samples, airborne suspended particulates (SPM) are measured by passing air at a high flow-rate of 1.1 to 1.7 cubic meters per minute through a high efficiency filter paper (Whatman 934-AH Glass Microfiber Filters) which retains the particles. The instrument measures the volume of air sampled, while the amount of particulates collected is determined by measuring the change in weight of the filter paper as a consequence of the sampling. In High Volume Sampler provisions have been made for simultaneous sampling of gaseous pollutants. Gaseous attachment (Fig: 3.3) contains three impinger bottles of 35 ml capacity for simultaneous absorption of different gaseous pollutants. Here the air is passed through suitable reagents that would absorb specific gases where gaseous pollutants like SO$_2$, NO$_x$, etc. are analyzed subsequently by simple wet chemistry method to determine the concentration of specific...
pollutant. The gaseous sampling requires only a few LPM (1-3 LPM) of air flow. This absorbing solution is placed within the impinger bottles placed in between ice cubes or cold water, for complete absorption of sparsely soluble gases. These absorbing solutions can then be taken directly to the laboratory for analysis.

**Fig 3.3: Gaseous attachment APM 411**

**VIS- Spectrophotometer**

The spectrum was taken with VIS Spectrophotometer (Helios UV-Visible Spectrophotometer single-beam spectrophotometer) (Fig: 3.5). The degradation studies were conducted by measuring absorbance in VIS spectrophotometer, having a wavelength range from 190-1100nm using a 1 cm glass cell. All the experiments reported were carried out in a 4 ml glass cuvette. The scan speed is 200 nm/min with a step of 1.0 nm. Wavelength resolution is 0.1 nm. A spectrophotometer is having both Tungsten and Deuterium lamp at operating temperature of 0-40°C.
Fig 3.4: System Configuration of gaseous extension with the HVS

Fig 3.5: Helios UV-Visible Spectrophotometer single-beam spectrophotometer
Weighing Balance: LIBROR AEG 2220, Shimadzu, capacity-220.0000g (Fig: 3.6)

Libror weighing balance was used for the filter paper weighing, having capacity of 220 g.

3.3 METHODOLOGY

The next step involves the air sampling for three pollutants which are PM 10, SO2, NO2 (Chauhan et al., 2010; Kumar et al., 2011) at all the selected sites so that the concentration at these points can be known. All the instruments required for sampling were taken to the first sampling site. Sampling at a particular site was done twice a week. All the instruments were shifted to the next site and the procedure was repeated again. Different precautions and procedures used for sampling of three parameters.
Various methods are available for the pollutant gases and the particulate pollutants.
The following methods are very sensitive ones yet percentage of errors are very less.
The methods prescribed for the gases SO\textsubscript{2}, NO\textsubscript{x} and the particulate pollutants PM\textsubscript{10} are: Modified West and Gaeke method, Modified Jacob Hochheiser, Cyclonic flow technique respectively.

3.4. DESCRIPTION OF METHODS

The methods used for the sampling of selected criteria pollutants are laid down by the CPCB (CPCB, AAQM, 2009)

3.4.1 MODIFIED WEST AND GAEKE METHOD FOR MEASUREMENT OF SO\textsubscript{2}

PRINCIPLE: Sulfur dioxide from the air is absorbed in a solution of potassium tetrachloromercurate (TCM) (Fig: 3.7). A Dichlorosulphomercurate complex, which resists oxidation by the oxygen in the air, is formed. Once formed, this complex is stable to strong oxidants such as ozone and oxides of nitrogen and therefore, the absorbing solution may be stored for some time prior to analysis. The complex is made to react with pararosaniline and formaldehyde to form the intensely colored pararosaniline methylsulphonic acid. The absorbance of the solution is measured by means of a suitable spectrophotometer. Concentration of sulfur dioxide in the range of 25-1050 μg/Cu-m can be measured under the conditions given are measured concentration below 25 μg/cu-m by sampling larger volumes of air, but only if, the absorber efficiency of the particular system is first determined and found to be satisfactory. Higher concentration can be analyzed by using smaller gas samples of a suitable aliquot of the collected
sampler. The beer's law is followed through the working range from 0.03 to 1.0 absorbance units. This corresponds to 0.8-27 µg of sulfate ion in 25 ml of final solution calculated as sulfur dioxide. The lower limit of detection of sulfur dioxide in 10 ml absorbing reagents is 0.75 µg based on twice the standard deviation, which represent a concentration of 25 µg/cu-m in an air sample of 30 liters. (Indian standard IS 5182 part2)

ANALYSIS:

A spectrophotometer suitable for measurement of absorbance at 560 nm with an effective spectral bandwidth of less than 15 nm is required. Reagent blank problems may occur with spectrophotometer having greater spectral bandwidths. The wavelength calibration of the instrument should be verified. If, transmittance is measured, this can be converted to the observance by the formula:

\[ A = 2 - \log T \]
REAGENS:

Sampling reagents:

(i) Water - High quality water was used. It must be free from oxidants, particularly chlorine, which may not be removed by distillation. This criterion must be observed whether water is prepared by distilling or deionizing or by using a combination of both techniques.

(ii) Absorbing Reagents, 0.04 M Potassium Tetrachloro mercurate (TCM) – Dissolve 10.86 g, mercuric chloride, 0.066 g EDTA, and 6.0 g potassium chloride or sodium chloride 4.68 gm in water and bring to the mark in a 1 litre volumetric flask. The pH of this reagent should be approximately 4.0 but, it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3. The absorbing reagent has been normally stable for six months. If, a precipitate forms, discard the reagent after recovering the mercury.

Analysis reagents

(i) Sulphamic Acid (0.6%) – Dissolved 0.6 g sulphamic acid in 100 ml distilled water. Prepare fresh daily.

(ii) Formaldehyde (0.2%) - Diluted 5 ml formaldehyde solution (36-38%) to 1 litre with distilled water. Prepare fresh daily.

(iii) Stock Iodine Solution (0.1 N) - 12.7 g iodine in a 250 ml beaker, added 40 g potassium iodide and 25 ml water. Stirred until all is dissolved, then dilute to 1 litre with distilled water.
(iv) Iodine Solution (0.01 N) - Prepared approximately 0.01 N iodine solution by diluting 50 ml of stock solution to 500 ml with distilled water.

(v) Starch Indicator Solution - Triturated 0.4 gm soluble starch and 0.002 g mercuric iodide preservative with a little water and add the paste slowly to 200 ml boiling water. Continue boiling until the solution is clear, cool, and transfer to a glass stopper bottle.

(vi) Stock, Sodium Thiosulfate Solution (0.1 N) - Prepared a stock solution by placing 25 g sodium thiosulfate pentahydrate in a beaker, add 0.1 g sodium carbonate and dissolve using boiled, cooled distilled water making the solution up to a final volume of 1 litre. Allow the solution to stand one day before standardizing. To standardize, accurately weigh to the nearest 0.1 mg, 1.5 g primary standard potassium iodate dried at 180°C, dissolve, and dilute to volume in a 500 ml volumetric flask. Into a 500 ml iodine flask, transfer 50 ml of iodate solution by pipette. Added 2 g potassium iodide and 10 ml of N hydrochloric acid and stopper the flask. After 5 min, titrate with stock thiosulfate solution to a pale yellow. Added 5 ml starch indicator solution and continue the titration until the blue color disappears. Calculated the normality of the stock solution.

(vii) Sodium Thiosulphate Titrant (0.01 N) - Diluted 100 ml of the stock thiosulfate solution to 1 litre with freshly boiled and cooled distilled water.

(viii) Standardized Sulphite Solution for Preparation of Working Sulphite-TCM Solution Dissolved 0.30 g sodium metabisulphite (Na$_2$S$_2$O$_5$) or 0.40 g sodium sulphite (Na$_2$SO$_3$) in 500 ml of recently boiled, cooled, distilled water.
Sulphite solution is unstable; it is, therefore, important to use water of the highest purity to minimize this instability. This solution contains the equivalent of 320-400 µg/ml of SO₂. The actual concentration of the solution is determined by adding excess iodine and back-titrating with a standard sodium thiosulfate solution. To back-titrate, measure, by pipette, 50 ml of the 0.01 N iodine solutions into each of two 500 ml iodine flasks A and B. To flask A (blank) add 25 ml distilled water and into flask B (sample) measure 25 ml sulphite solution by pipette. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulphite-TCM solution at the same time iodine solution is added to the flasks. By means of a burette containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml starch solution and continue the titration until the blue color disappears.

(ix) Working Sulphite-TCM Solution - Measured 2 ml of the standard solution into a 100 ml volumetric flask by pipette and bring to mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution in micrograms of sulfur dioxide per milliliter. This solution is stable for 30 days if kept in the refrigerator at 5 °C. If not kept at 5 °C, prepare fresh daily.

(x) Purified Pararosaniline Stock Solution (0.2% Nominal)

a. Dye Specifications - The pararosaniline dye must meet the following specifications:

b. The dye must have a wavelength of maximum absorbance at 540 nm when assayed in a buffered solution of 0.1 M sodium acetate- acetic acid.
c. The absorbance of the reagent blank, which is temperature sensitive to the extent of 0.015 absorbance unit/°C, should not exceed 0.170 absorbance unit at 22°C with a 1 cm optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye.

d. The calibration curve should have a slope of 0.030 ± 0.002 absorbance unit/µg SO₂ at this path length when the dye is pure and the sulphite solution is properly standardized.

(xi) Pararosaniline Stock Solution - Dissolved 0.500 gm of specially purified pararosaniline (PRA) in 100 ml of distilled water and keep for 2 days (48 hours). Pararosaniline Working Solution - 10 ml of stock PRA is taken in a 250 ml volumetric flask. Add 15 ml conc. HCL and make up to volume with distilled water.

PROCEDURE:

Sampling and Analysis

Sampling - Procedures are described for short-term (4 hours) long-term (8 hours, 24 hours) sampling. Here we have taken 8 hours for gaseous as well as particulate sampling. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the range in question.

8 Hours Sampling - Inserted a midget impinger into the sampling system. Add 10 ml TCM solution to the impinger (30 ml TCM solution for 4 hours sampling).
Collect sample at 1 litre/minute for 30 minutes, 1 hour or 4 hours using either a rotameter, or a critical orifice, to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil to prevent deterioration. Determine the volume of air sampled by multiplying the flow rate by the time in minutes and record the atmospheric pressure and temperature. Remove and stopper the impinger. If, the sample must be stored for more than a day before analysis, keep it at 5°C in a refrigerator; during hot weather, sampling is not recommended unless it is possible to refrigerate the samples as taken.

Fig 3.8: SO2 analysis flow chart

Sample Preparation - After collection, if a precipitate is observed in the sample, remove it by centrifugation.
8 Hours Samples - Transfer the sample quantitatively to a 30 ml volumetric flask using about 5 ml distilled water for rinsing. Delay analyses for 20 minutes to allow any ozone to decompose.

Sample Preservation

After sample collection, the solutions were stored at 5 °C in a refrigerator. At 22 °C losses of sulfur dioxide occur at the rate of 1% per day. When samples are stored at 5 °C for 30 days, no detectable losses of sulfur dioxide occur. The presence of EDTA enhances the stability of sulfur dioxide in solution, and the rate of decay is independent of the concentration of sulfur dioxide.

Determination:

For each set of determinations prepared a reagent blank by adding 10 ml of the unexposed TCM solution to a 25 ml volumetric flask. Prepared a control solution by measuring 2 ml of working sulphite-TCM solution and 8 ml TCM solution into a 25 ml volumetric flask by pipette. To each flask containing either sample, control solution, or reagent blank, added 1 ml 0.6% sulphamic acid and allowed to react 10 minutes to destroy the nitrite resulting from oxides of nitrogen. Measured by pipette and added 2 ml of 0.2% formaldehyde solution and 2 ml pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 minutes and before 60 minutes, determine the absorbance of the sample, A, reagent blank, A₀, and the control solution at 560 nm using cells with a 1 cm path length. Use distilled water; not the reagent
blank, as the optical reference. This is important because of the color sensitivity of the reagent blank to temperature changes which may be induced in the cell compartment of a spectrophotometer. Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol and clean pipe cleaner after use. If, the temperature of the determinations does not differ by more than 2 °C from the calibration temperature, the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve. If, the reagent blank differs by more than 0.03 absorbance unit that found in the calibration curve, prepare a new curve.

Absorbance Range

If, the absorbance of the sample solution lies between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to six fold with the reagent blank in order to obtain on-scale readings within 10% of the true absorbance value.

Calibration and Efficiencies

(i) Calibration Curve - Procedure with Sulphite Solution - Measured by pipette graduated amounts of the working sulphite-TCM solution (such as 0, 0.5, 1, 2, 3 and 4 ml) into a series of 25 ml volumetric flasks. Added sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then added the remaining reagents as described in previous sections. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within + 1 °C and within the range of 20-30 °C. The temperature of calibration must be maintained within two degrees. Plotted the
absorbance against the total concentration in micrograms sulfur dioxide for the corresponding solution. The total micrograms sulfur dioxide in solution equals the concentration of the standard in micrograms sulfur dioxide per milliliter times the milliliter of sulphite solution added (µg SO₂ = µg/ml/SO₂ x ml added). A linear relationship should be obtained, and the Y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal, and denote as B, the calibration factor. See previous section for specifications on the slope of the calibration curve. This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO₂ for each series of determinations is recommended to ensure the reliability of this factor.

(ii) Sampling Efficiency - Collection efficiency is generally above 98%; efficiency may fall off, however, at concentrations below 25 µg/cu-m.

CALCULATION:

Normality of Thiosulfate Solution

The normality of this solution N is calculated as follows:

\[ N = \frac{W \times 10^3 \times 0.1}{V \times 35.67} \]

Where:
V - Volume thiosulfate used, ml
W - Weight of potassium iodate, g
35.67 - Equivalent weight of potassium iodate

Concentration of Sulphite Solution

The amount of sulfur dioxide per milliliter in the standard solution, is calculated as

\[
C = \frac{(V_1-V_2) \times N \times K}{V}
\]

Where:

C - SO2 concentration in \( \mu g/ml \)
V1 - Volume of thiosulfate for blank, ml
V2 - Volume of thiosulfate for sample, ml
N - Normality of thiosulfate
K - 32000 (Milliequivalent weight SO2/\( \mu g \))
V - Volume of standard sulphite solution, ml

Sulfur Dioxide Concentration at the Reference Conditions

When sulphite solutions are used to prepare calibration curves, compute the concentration of sulfur dioxide, C, in micrograms per cubic meter, in the sample as follows:

\[
C = \frac{(A - A_o) \times 10^3 \times B}{V \times D}
\]
The Concentration of SO2 in µg/cu-m in the sample is calculated as follows:

\[
C (SO2 \, \mu g/cu-m) = \frac{(A - A_0) \times 10^3 \times B}{V}
\]

Where:
- A - Sample absorbance
- A₀ - Reagent blank absorbance
- \(10^3\) - Conversion of liters to cubic meters
- V - Volume of air sampled in liters
- B - Calibration factor, µg/absorbance unit
- D - Dilution factor

Conversion of Micrograms per Cubic Metre to Parts per Million

If desired, the concentration of sulfur dioxide may be calculated as parts per million of sulfur dioxide at reference conditions as follows:

\[
ppm \, SO_2 = \frac{\mu g \, SO_2/cu-m \times 3.82 \times 10^4}{10^3}
\]
3.4.2 MODIFIED JACOB AND HOCHHEISER METHOD FOR DETERMINATION OF NO\textsubscript{x} IN THE ATMOSPHERE


PRINCIPLE:

Ambient nitrogen dioxide (NO\textsubscript{2}) is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite (Fig: 3.8). The concentration of nitrite ion (NO\textsubscript{2}) produced during sampling is determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide, and N-(1-naphthyl) -ethylenediamine dihydrochloride (NEDA) and measuring the absorbance of the highly colored azodye at 540 nm. The nominal range of the method is 9 to 750 µg NO\textsubscript{2}/cu-m (0.005 to 0.4 ppm). The range of the analysis is 0.04 to 2.0 µg NO\textsubscript{2}/ml, following Beer's Law throughout this range (0 to 1.0 absorbance units). Under the specified conditions of 50 ml of absorbing reagent, a sampling rate of 200 cu-cm /min for 24 hours, and a sampling efficiency of 0.82, the range of the method is, therefore, 9 to 420 µg/NO\textsubscript{2}/cu-m (0.005 to 0.22 ppm). Nitrogen dioxide concentrations in the range of 420 to 750 µg/cu-m (0.22 to 0.4 ppm) are accurately measured by 1:1 dilution of the collected sample. Based on results from a collaborative study, the within laboratory standard deviation is 8 µg/cu-m (0.004 ppm) and the between laboratory standard deviation is 11 µg/cu-m (0.006 ppm) over the range of 50 to 300 µg NO\textsubscript{2}/cu-m (0.027 to 1.16 ppm). Based on results from a collaborative study, the method has an average bias of -3% over the range of 50 to 300 µg NO\textsubscript{2}/cu-m (0.027 to 0.16 ppm).
Fig 3.9 NOx analysis principle

INTERFERENCES:

Nitric oxide (NO) is a positive interference and carbon dioxide (CO₂) is a negative interference. The average error resulting from normal ambient concentrations of NO and CO₂ is small for most monitoring situations and does not necessitate applying a correction to measurements obtained with the method. Potential interference from sulfur dioxide (SO₂) is eliminated by converting any SO₂ to sulfate with hydrogen peroxide during analysis.

SAMPLE PRESERVATION:

Collected samples are stable for at least six weeks at room temperature. Stored samples should be tightly sealed to prevent absorption of NO₂ from the atmosphere.
ANALYSIS

Sampling Reagents:

(i) Distilled Water - Must be reagent water as defined by ASTM procedure 1193-66 part 6.3 (consumption of potassium per-magnate test).

(ii) Sodium Hydroxide.

(iii) Sodium Arsenite - CAUTION: Arsenic compounds are highly toxic and everybody should handle with extreme care. Must avoid contact with skin and especially with eyes. Avoid generating dust or breathing dust. Keep away from food. Wash hands after handling it. Do not take internally.

(iv) Absorbing Reagents - Dissolved 4.0 g of sodium hydroxide in distilled water, added 1.0 g of sodium arsenite, and diluted to 1,000 ml with distilled water.

Analysis reagents

(i) Sulfanilamide - Melting point 165 to 167 °C.

(ii) N-(1-Naphthyl)-ethylenediamine Di-hydrochloride (NEDA) - A 1% aqueous solution should have only one absorption peak at 320 nm over the range of 260-400 nm. NEDA showing more than one absorption peak over this range is impure and should not be used.

(iii) Hydrogen Peroxide, 30%.

(iv) Phosphoric Acid, 85%.

(v) Sulfanilamide Solution - Dissolved 20 g of sulfanilamide in 700 ml of
distilled water. Added, with mixing, 50 ml of 85% phosphoric acid and
diluted to 1,000 ml. This solution is stable for one month, if refrigerated.

(vi) NEDA Solution - Dissolved 0.5 g of NEDA in 500 ml of distilled water.
This solution is stable for one month, if refrigerated and protected from light

(vii) Hydrogen Peroxide Solution - Diluted 0.2 ml of 30% hydrogen peroxide to
250 ml with distilled water. This solution may be used for one month, if,
refrigerated and protected from light.

PROCEDURE

Preparation of Calibration Graph.

Sodium Nitrite - Assay of 97% NaNO₂ or greater.

Sodium Nitrite Stock Solution (1000 μg NO₂/ml) - Dissolved 1.5 g of desiccated
sodium nitrite in distilled water and dilute to 1,000 ml such that a solution containing
1000 μg NO₂/ml is obtained. The amount of NaNO₂ to be used if the assay percent is less than 100%, is calculated as follows:

\[
\frac{1.500}{A} = G
\]

Where:

- \( G \) = Amount of NaNO₂, grams
- 1.500 = Gravimetric conversion factor
- \( A \) = Assay, percent (should be 97 or greater)

This stock solution can be stored for six weeks, if refrigerated.

Sodium Nitrite Working Standard (1.0 μg NO₂/ml)

Solution A - Pipette 5 ml of the stock solution into a 500 ml volumetric flask and diluted to volume with distilled water. This contains 10 μg NO₂/ml.

Solution B - Pipettes 25 ml of solution A into a 250 volumetric flask and diluted to volume with absorbing solution. This contains 1 μg NO₂/ml. Prepared fresh daily.

Calibration

Flowmeter - Calibrated the flowmeter against a calibrated flow measurement standard, such as a wet test meter, bubble, flow meter, or other reliable volume measurement standard. Calibrate in units of standard cm³/min (i.e., corrected to 25 °C and 760 torr).

Absorber - Calibrated the polypropylene absorber pipeting 50 ml of water or absorbing
reagent into the absorber. Scribe the level of the meniscus with a sharp object, mark over the area with a felt-tip marking pen, and rub off the excess.

Spectrophotometer

Prepared calibration curve using 1 µg/ml working standards. In accordance with the analytical procedure given in, measure and record the absorbance for each calibration standard (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20 µg NO₂). Plotted absorbance (y-axis) versus the corresponding concentration in µg NO₂/50 ml final solution (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve.

Sample Collection

Sampling

Assemble the sampling apparatus at the sampling site. Components upstream from the absorber may be connected, where required, with Teflon tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with Teflon or polypropylene. 30 ml absorbing reagent added exactly of to the calibrated absorber. Disconnect the funnel, connect the calibrated flowmeter, measure the flow rate before sampling and record as F1. If, the flow rate before sampling is not 0.2 Lpm, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate of 0.2 Lpm. Sample for 8 hrs. Recorded the exact sampling time in minutes at ts.

Measured the flow rate after the sampling and record as Ff.

Sealed the collected samples and transport to the laboratory for analysis.
Analysis

We have to replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorber. Mix thoroughly.

Pipette 10 ml of the collected sample into a test tube. Pipette in 1 ml of hydrogen peroxide solution, 10 ml of sulfanilamide solution, and 1.4 ml of NEDA solution, with thorough mixing after the addition of each reagent and make up to 50 ml with distilled water. Prepare a blank in the same manner using 10 ml of unexposed absorbing reagent. After a 10 min, color development interval, measure and record the absorbance at 540 nm against the blank. Determine μg NO₂ from the calibration curve. Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot of the collected samples with an equal quantity of unexposed absorbing reagent. A randomly selected 5-10% of the samples should be analyzed as a part of an internal quality assurance program.

CALCULATION:
Air Volume - Calculate the volume of air samples as follows:

\[
V = \frac{F_1 + F_f}{2} \times ts \times 10^{-3}
\]

Where:

\( V = \) Volume of air sample, cu-m

\( F_1 = \) Air flow rate before sampling, litre/min

\( F_f = \) Air flow rate after sampling, litre/min

\( ts = \) Sampling time, min

\( 10^{-3} = \) Conversion of lpm to cubic-m.
If, the temperature and pressure conditions at the time of the initial and final air flow rate measurements are substantially different from the conditions under which the flowmeter was calibrated, appropriate corrections to the flow rate measurements may be made to improve the accuracy of the resultant NO₂ concentration measurement. The mathematical form of these corrections depends on the type of flowmeter used; consult an appropriate reference for guidance.

NO₂ Concentration in Analyzed Sample - Determine µg NO₂/ml graphically from the calibration curve or compute from the slope and intercept values.

NO₂ Concentration in Air Sample - Calculate as µg of NO₂ per cubic meter of air as follows:

\[
\frac{\mu g \text{NO}_2 \times V_s}{\mu g \text{NO}_2/\text{cu-m}} = \frac{\mu g \text{NO}_2 \times V_s}{V_a \times 0.82} \times D
\]

Where:

- \( \mu g/\text{NO}_2 \) = NO₂ concentrations in analyzing samples
- \( V_a \) = Volume of air sample, cu-m
- 0.82 = Sampling efficiency
- \( D \) = Dilution factor (\( D = 1 \) for no dilution; \( D = 2 \) for 1:1 dilution).
- \( V_s \) = Volume of sampling solution

The NO₂ concentration may be calculated as ppm using: ppm

\[
\text{NO}_2 = (\mu g \text{NO}_2/\text{cu-m}) \times 5.32 \times 10^{-4}
\]
3.4.3 MEASUREMENT OF RESPIRABLE SUSPENDED MATTER (PM10) BY CYCLONIC FLOW TECHNIQUE

Method for measurement of Respirable Suspended Particulate Matter (PM10) in ambient air (Cyclonic Flow Technique).

PRINCIPLE: Air is drawn through a size-selective inlet and through a 20.3 x 25.4 cm (8 x 10 in) filter at a flow rate which is typically 1132 L/min (Fig: 3.10). Particles with aerodynamic diameter less than the cut-point of the inlet are collected by the filter. The mass of these particles is determined by the difference in filter weights prior to and after sampling. The concentration of PM10 in the designated size range is calculated by dividing the weight gain of the filter by the volume of air sampled. This method is applicable for measurement of PM10 in the ambient air.

Fig 3.11 High volume sampler construction
INTERFERENCES:

Passive Deposition- Passive deposition occurs when windblown dust deposits on a filter both prior to and after sampling.

Recirculation- recirculation occurs when the blower exhaust, which contains carbon and copper particles from the armature and brushes, is entrained in the sample air.

Positive biases of 0.15μg/cu-m have been measured, which are insignificant mass interferences, but which may affect carbon and copper measurements. Recirculation can be minimized by assuring a tight seal between the blower and the sampler housing or by ducting the blower exhaust away from the sampler.

Filter Artifact Formation – Sulfur dioxide, nitrogen oxides, nitric acid and organic vapors can be absorbed on the filter medium along with the suspended particles thereby causing positive biases. Samples taken in the presence of high SO2 concentrations have been shown to yield up to 10 μg/m³ of excess sulfate on glass fiber filters.

Filter Conditioning – Filter conditioning environments can result in different mass measurements as a function of relative humidity (RH). Soluble particles take on substantial quantities of water as RH increases, especially above the deliquescence point of approximately 70% RH. Increased mass deposits of 50% or more have been observed as RH increases to 100%. Twenty-four hours at a constant temperature and RH is considered adequate for sample equilibration.
Shipping Losses – Particle loss during transport occurs when filters are heavily loaded with large dry aerosols. It is more prevalent on membrane than on glass fiber filter. Particle loss is minimized by shorter sample duration in heavily polluted environments, use of fiber as opposed to membrane filters, folding the filter prior to transport, and careful shipping procedures.

Precision and Accuracy- Mass of the filter deposit, the flow rate through the filter, and sampling time have a typical precision of +2 mg, +5%, and +1 min, respectively, as determined from performance tests. The accuracy of those measurements can be well within these tolerances when determined by independent standards. These uncertainties combine to yield a propagated precision of approximately +13% at 10 µg/m³ and approximately +5% at 100 µg/m³. The filter deposit mass measurement precision dominates at low concentrations while the flow rate precision dominates at high concentrations.

APPARATUS

Inlet for PM10 Sampling-

Cyclonic Flow Inlet (Fig: 3.10)

Cyclones use centrifugal force to remove dust. A particle in a rotating air stream is subjected to a centrifugal force that accelerates it towards a surface where it will impact and lose momentum, thus being removed from the air stream. In a typical cyclone pre-collector, the air enters tangentially at its side and swirls around inside. Particles above 10 µm are thrown to the cyclone walls and collected at its base ("grit-pot"). The air
containing the reparable dust, leaves through the central exit at the top of the cyclone and is filtered to collect the dust on a filter paper. The sampling effectiveness of this inlet varies depending on its orientation with respect to wind direction and on the wind speed (Mcfari et al., 1979, Wedding, J.B et al., 1977).

Flow Controllers

Manual Volume Flow Control - A variable voltage transformer placed in series with the blower controls the blower motor power. The motor speed varies with the voltage supplied, and the flow rate through a filter can be adjusted by increasing or decreasing the voltage to obtain the desired value of the resistance of the filter being used. The flow rate decreases as filter deposit increases, but this change is normally less than 10% and is quantifiable via pre- and post-exposure flow measurements.

Laboratory Equipment

Controlled Environment - A clean laboratory environment is required for filter inspection, equilibration, and weighing. A temperature in the range of 15 to 30°C with ± 3°C variability (Countess. R.J., 1974, Chow, I.C 1980) and a relative humidity of 20 to 45% with ± 5% variability is recommended (Countess. R.J., 1974).

Analytical Balance - The balance must be equipped with an expanded weighing chamber to accommodate 20.3 x 25.4 cm (8 x 10 in) filters and must have a sensitivity of 0.1 mg.

Numbering - Though filter ID numbers can be written on the edge of filters with a pen.

Wet Bulb/Dry Bulb Psychomotor - The temperature and relative humidity of the
controlled filter processing environment is measured and recorded before and after each filter processing session. Adjustments are made to the environmental control system when equilibration conditions exceed pre-set tolerances.

Calibration and Auditing Equipment

Primary Flow Rate Standard - A positive volume displacement device serves as a primary standard. A spirometer, a "frictionless" piston meter, or a Roots meter can serve as such a standard.

Orifice Transfer Standard - The PM10 sampler calibration orifice consists of a 3.175 cm (1.25 inch) diameter hole in the end cap of 7.62 cm (13 in) diameter by 20.3 cm (8 in) long hollow metal cylinder. This orifice is mounted tightly to the filter support in place of the inlet or at the cyclone inlet during calibration. A small tap on the side of the cylinder is provided to measure the pressure drop across the orifice. A flow rate of 1132 L/min through the orifice typically results in a pressure difference of several inches of water. The relationship between pressure difference and flow rate is established via a calibration curve derived from measurements against a primary standard such as a rootsmeter at standard temperature and pressure. Flow resistances that simulate filter resistances are introduced at the end of the calibrator opposite the orifice by a set of perforated circular disks.

Manometer - A calibrated pressure gauge or water manometer spanning 0 to 15 inches of water (0-4 kPa) is used to determine the pressure drop across the orifice.
Barometer - The atmospheric pressure at the time of calibration and at the time of measurement is determined with a barometer. Flow rate corrections are made if, these two pressures differ by more than 5 kPa (4% of standard 101.3 kPa).

Thermometer - The atmospheric temperature at the time of calibration and at the time of measurement is determined with a thermometer. Flow rate corrections are made if, these two temperatures differ by more than 15°C (5% of standard 298 K).

Class-S Weights - A 3g standard mass of Class-S or Class-M quality is used to verify the span of the analytical balance.

Analytical Balance - Some analytical balances can be calibrated by the operator while others require specialized skills to re-calibrate. In general, analytical balances should be calibrated when first purchased, any time the balance is moved, at least every twelve months, or whenever an NBS traceable 3.0000 g weight registers outside ± 0.5 mg of its designated weight. At each weighing session a balance calibration check is performed using a Class S of Class M weight.

REAGENTS

Filter Media - A 20.3 x 25.4 cm (8 x 10 in) glass fiber filter is used to collect particles. The choice of filter type results from a compromise among the following filter attributes (i) mechanical stability, (ii) chemical stability (iii) particle sampling efficiency, (iv) flow resistance, (v) clogging level, (vi) blank values (vii) artifact formation, and (viii) cost and availability. EPA filter requirements specify 0.3 μm DOP sampling efficiency in excess of 99%, weight losses or gains due to mechanical or chemical instability of less than a 5
μg/m³ equivalent, and alkalinity of less than 25 micro-equivalent/g to minimize sulfur
dioxide (SO₂) and nitrogen oxides (NOx) absorption (EPA, 1987). The most appropriate
filter media for high volume sampling are cellulose fiber, glass fiber, quartz fiber, Teflon
coated glass fiber, and Teflon membrane. None of these materials is perfect for all
purposes.

Glass fiber filters meet requirements in most categories with the exception of artifact
formation and blank levels. Sampling efficiency is very high for all particle sizes
(Lippman, M. 1983, Schleien, B. et al., 1966). Blank levels for several elements of
interest are high and variable (Chow, I.C 1980, Cadle, S.H. et al., 1983). Glass fiber
filters may exhibit organic carbon artifacts.

Filter Jacket - A smooth, heavy paper folder or envelope is used to protect the filter
between the lab and field and during storage. Filter and sampling data are often recorded
on the outside of the jacket, but this should not be done while the filter is in the jacket to
prevent damage.

PROCEDURE

Figure 3.11: Flow diagram of the routine operating procedure described in the following
sub-sections.

Filter Inspection - Clean the light table surface with a methanol soaked wiper and allow it
to dry. Filters should be handled with flowed hands to prevent contamination. Place each
filter on the light table and examine it for pinholes, loose particles, tears, creases, lumps,
or other defects. Loose particles may be removed with a soft brush. Filters not meeting
visual criteria should not be used. If chemical analyses are to be performed, one or two filters from each lot should be analyzed for blank levels and the lot should be rejected if pre-set specifications are not met.

**Fig: 3.12 Flow chart of PM10 Sampling**

Filter Identification - Apply an ID number in the upper right hand corner on the smoothest side of each filter with the incrementing number machine. Gentle pressure
must be used to avoid damaging the filter. Record this number in a chain-of-the custody log book and on a filter jacket. The chain-of-custody log book contains columns opposite every filter ID to record dates and technician initials for filter inspection, equilibration, pre-weighing, shipment to field, receipt from the field, re-equilibration, post-weighing and storage. These records identify the disposition of each sample and prevent the creation of two samples with the same ID.

Filter Equilibration - Place blank or exposed filters in a storage rack in the controlled temperature and relative humidity environment (15 to 27°C and 0 to 50%, relative humidity) for 24 hours prior to weighing. The rack should separate filters such that all surfaces are exposed to the equilibration environment. Measure the temperature and relative humidity of the controlled environment and record the values in the equilibration column of the chain-of-custody log book.

Filter Weighing - It is best to weigh filters in groups of ten to fifty. Wear gloves for all filter handling. Stack filter jackets with data forms printed on them in the same order (in ascending order of filter ID numbers, if possible) as the order of filters in the equilibration rack. Adjust the balance tare to read zero with nothing in the weighing chamber and adjust the span to read (or verify that it reads) 3.00000 g with the 3 g standard weight on the weighing pan. Place a filter in the weighing chamber and adjust the balance to its equilibrium position. If, a stable reading cannot be obtained, it may be necessary to neutralize electrostatic charges with a radioactive source prior to and during weighing. Record the weight on the data form in the blank or exposed filter column. Verify the zero and span every ten filters. If, these differ from their normal values by
more than ± 1.0 mg, read just them and re-weight the previous ten filters. Place each filter in its filter jacket when weighing is complete, but do not seal the jacket opening. A separate technician randomly selects four filters or ten percent of all filters in the batch (whichever is larger), re-weight them and subtracts this check-weight value of the corresponding routine weight. If, any check weight differs by more than ± 4.0 mg from the routine weight, re-weight the entire batch of filters. Seal filter jackets and ship blank filters to the field or place exposed filters into storage.

Field Sampling - Tilt back the inlet and secure it according to manufacturer's instructions. Loosen the face-plate wing-nuts and remove the face plate. Remove the filter from its jacket and center it on the support screen with the rough side of the filter facing upwards. Replace the face-plate and tighten the wing-nuts to secure the rubber gasket against the filter edge. Gently lower the inlet. Inertial jet and cyclonic inlets must have their seals in contact with the top of the face-plate. Look underneath the inlet just as it is coming into contact with the face-plate to assure that this contact is being made. It may be necessary to readjust the position of the filter/motor assembly in the sampler housing to obtain such a seal. Excessively windy and wet conditions should be avoided when changing samples. Pre-loading in a filter cartridge assembly, temporary removal of the sampler to a protected area, or a wind or rain shield may be used if, the sample must be changed in inclement weather. Set the timer for the desired start and stop time. Replace the chart paper in the flow recorder, if there is one, set the proper time, and mark the time and date on the chart. For a manual flow controlled sampler turn on the motor for five minutes and measure the exhaust pressure with a pressure gauge or Rotameter. Read the flow rate corresponding to this exhaust pressure from the calibration curve and
record it on the data sheet. Turn off the motor and assure that the timer is in its automatic mode. For automatically flow-controlled units, record the designated flow rate on the data sheet. Record the reading of the elapsed time meter. The specified length of sampling is commonly 8 hours or 24 hours. During this period, several readings (hourly) of flow rate should be taken. After sampling is complete, record the final flow rate and the elapsed time in the same manner. Subtract the initial elapsed time from the final elapsed time to determine the sample duration. Remove the face-plate by removing the wing-nuts. Fold the filter in half lengthwise by handling it along its edge with the exposed side inward. Insert the filter in its jacket. Note the presence of insects on the deposit, loose particles, non-centered deposits, evidence of leaks, and unusual meteorological conditions on the data sheet. Mark the flow recorder chart, if any, and return it with the data sheet.

CALCULATIONS

Calculation of Volume of Air Sampled

\[ V = QT \]

\[ V = \text{Volume of air sampled in m}^3 \]

\[ Q = \text{Average flow rate in m}^3/\text{minute} \]

\[ T = \text{Total sampling time in minutes} \]

Calculation of Suspended Particulate Matter in Ambient Air

\[ SPM = \frac{(W_f - W_i) \times 10^6}{V} \]
Where:

\[ SPM = \text{Mass concentration of suspended particles in } \mu g/m^3 \]
\[ W_i = \text{Initial weight of filter in g.} \]
\[ W_f = \text{Final weight of filter in g.} \]
\[ V = \text{Volume of air sampled in } m^3 \]
\[ 10^6 = \text{Conversion of g to } \mu g \]

In the above study, the statistical methods were, for quantitative data, descriptive statistics was presented by N, Mean, Standard Deviation and Range. For qualitative data, frequency count N and percentage were put in a tabular manner.

To analyze the data, an appropriate statistical tests were applied such as Test of Homogeneity of Variances, One way ANOVA- testing equality of variances of each pollutant for three years at each site– F test was used. Other data displayed by various tables and charts by using Microsoft excel (windows 7). The all statistical analysis had been done by using statistical software SPSS (version 16.0).

The test of significance was considered at the level *Significant at \( p < 0.05 \), ** very significant at \( p < 0.01 \), *** highly significant at \( p < 0.001 \).