CHAPTER 2

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The ambient air quality monitoring was carried out as per the official guidelines laid down and approved by the Central Pollution Control Board, New Delhi (CPCB, 2001)

2.1 Method for Determination of Suspended Particulate Matter (SPM) in the Atmosphere using High Volume Method

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 (40ft³/min). Particles with aerodynamic diameters 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 suspended particulate matter in the designated size range is calculated by dividing the weight-gain of the filter by the volume of air sampled (Robson and Foster, 1962; Olin and Kurz, 1975 and Rehme et al, 1984)

Other Analysis - Depending on the type of filter media used, filter samples can be analyzed for lead, iron, organic and elemental carbon, extractable organic material, elements, radioactive materials, inorganic compounds, and single particles.

Range and Sensitivity
a. Lower Quantifiable Limit - For 24-hour sample duration at 1132 L/min, the detection limit is determined by the reproducibility of the filter weight difference which shows a standard deviation (sigma) of approximately +/- 2mg. The three-sigma detection limit is 3.5μg/m³ approximately. The three-sigma lower quantifiable limit depends on the filter used and may be as high as 5μg/m³.

b. Upper Quantifiable Limit - For 24-hour sample duration at 1132 L/min, this limit is in the range of 400 to 1000μg/m³. The exact value depends on the nature of the aerosol being sampled: very small particles will clog the filter at a relatively low mass loading while larger particles will fall off during sample transport at high concentrations.
c. **Passive Deposition** - Passive deposition occurs when windblown dust deposits on a filter both prior to and after sampling.

d. **Inlet Loading and Re-Entrainment** - Material collected in size-selective inlets can become re-entrained in the sample flow. Controlled studies are insufficient to quantify this interference. It can be minimized by greasing or oiling inlet impaction surfaces, though this may change the size selective properties.

e. **Re-circulation** - Re-circulation occurs when the blower exhaust, which contains carbon and copper particles from the armature and brushes, is entrained in the samples air. Positive biases of $0.15\mu g/m^3$ have been measured (Countess, 1974; King and Toma, 1975), 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 blower exhaust away from the sampler.

f. **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 SO$_2$ concentrations have been shown to yield up to $10\mu g/m^3$ of excess sulfate on glass fiber filters. (Coutant, 1977 and Appel et al, 1984)

g. **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 (Tang, 1980). Increased mass deposits of 50% or more have been observed as RH increases to 100% (Tierney and Connor 1967). Twenty-four hours at a constant temperature and RH is considered adequate for sample equilibration.

h. **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 filters. 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, flow rate through the filter, and sampling time have typical precision of +/- 2 mg, +/- 5%, and +/- 1 min, respectively, as determined from performance tests (Muller et al, 1983). The accuracy of those measurements can be well within these tolerances when determined with independent standards. These uncertainties combine to yield a propagated precision of approximately +/- 13% at 10µg/m$^3$ and approximately +/- 5% at 100µg/m$^3$. The filter deposit mass measurement precision
dominates at low concentrations while the flow rate precision dominates at high concentrations.

Apparatus

a. Sampler - The essential features of a typical high volume sampler are shown in diagram of Figure 1 and 2. It is a compact unit consisting a protective housing, blower, voltage stabilizer, automatic time and time totalizer, rotameter, gaseous sampling assembly, filter holder capable of supporting a 20.3 x 25.4 cm, glass fibre filter.

b. Size -Selective Inlets

Peaked Roof Inlet (Figure - 2) - The peaked roof inlet is the oldest inlet and consists of a right triangular structure with an open hypotenuse placed over the filter. Over 50% of the particles smaller than 30 um to 50 um diameter penetrate this inlet (at 566 to 1698 L/min flow rates) and deposit on the filter (Mcfari et al, 1979 and Wedding et al, 1977). The peaked roof inlet does not have a sharp sampling effectiveness curve and is intended primarily to protect the filter from dust-fall. 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)

Figure 1: Interior Sketch Diagram of a High Volume Sampler
c. 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 for 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.

d. Laboratory Equipment

1. 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, 1974; Chow and Watson, 1980) and a relative humidity of 20 to 45% with +/- 5% variability is recommended (Countess, 1974).

2. Light Table - A photographic slide viewing table is used for filter inspection. 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.
3. **Equilibration Rack** - This rack separates filters from one another so that the equilibration air can reach all parts of the filter surface. A photograph record rack serves this purpose well.

4. **Numbering Machine** - Though filter ID numbers can be written on the edge of filters with a pen, an incrementing numbering machine that prints 4 to 8 digit ID numbers is more efficient and is less likely to damage the filter.

5. **Wet Bulb/Dry Bulb Psychrometer** - 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.

e. **Calibration and Auditing Equipment**

1. **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.

2. **Orifice Transfer Standard** - The high volume sampler calibration orifice consists of a 3.175 cm (1.25 in) 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 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 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.

3. **Manometer** - A calibrated pressure gauge or water manometer spanning 0 to 15 inches of water (0-4 k Pa) is used to determine the pressure drop across the orifice.

4. **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 k Pa (4% of standard 101.3 k Pa).

5. **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).

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

7. **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 or Class-M weight.

f. **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/gram 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 (Lippmann, 1983 and Schleien et al, 1966). Blank levels for several elements of interest are high and variable (Chow and Watson, 1980). 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 presents a flow diagram of the routine operating procedure described in the following Sub-sections.

a. **Filter Inspection** - Clean the light table surface with a Methanol soaked wiper and allow it to dry. Filters should be handled with gloved 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.

b. **Filter Identification** - Apply an ID number to 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-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 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.

c. **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.

d. **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-weigh 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-weigh them and subtracts this check-weight value from the corresponding routine weight. If any check weight differs by more than ±4.0 mg from the routine weight, re-weigh the entire batch of filters. Seal filter jackets and ship blank filters to the field or place exposed filters into storage.

e. **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 faceplate. 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 manually 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 reading (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.
**Figure 3: Flow Diagram for High Volume Operations**

**Calculation**

**Calculation of Volume of Air Sampled**

\[ V = QT \]

Where, \( V \) = Volume of air sampled in \( m^3 \); \( Q \) = Average flow rate in \( m^3/minute \); \( T \) = Total sampling time in minute
Calculation of Suspended Particulate Matter in Ambient Air

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

Where, \( SPM \) = Mass concentration of suspended particles in \( \mu g/m^3 \); \( W_i \) and \( W_f \) are initial and final weights of filter in g, respectively; \( V \) = Volume of air sampled in \( m^3 \); \( 10^6 \) = Conversion of g to \( \mu g \).

2.2 Method for determination of Nitrogen Dioxide in the Atmosphere

(Sodium Arsenite method)

Principle

Ambient nitrogen dioxide (NO\(_2\)) is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion (NO\(_2^-\)) produced during sampling is determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide, and N-(1-naphthyl)-ethylenediamine di-hydrochloride (NEDA) and measuring the absorbance of the highly colored azo-dye at 540 nm.

The nominal range of the method is 9 to 750 \( \mu g \) NO\(_2\)/m\(^3\) is 0.005 to 0.4 ppm (Jacob and Hochheiser, 1958). The range of the analysis is 0.04 to 2.0 \( \mu g \) NO\(_2\)/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 cm\(^3\)/min for 24 hours, and a sampling efficiency of 0.82, the range of the method is, therefore, 9 to 420 \( \mu g/NO_2/m^3 \) (0.005 to 0.22 ppm). Nitrogen dioxide concentrations in the range of 420 to 750 \( \mu g/m^3 \) (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 method has an average bias of -3% over the range of 50 to 300 \( \mu g \) NO\(_2\)/m\(^3\) (0.027 to 0.16 ppm).

Scope - This method is applicable to 24 hours integrated sampling of NO\(_2\) in ambient air.

Interferences-

Nitric oxide (NO) is a positive interferant and carbon dioxide (CO\(_2\)) is a negative interferant. The average error resulting from normal ambient concentrations on NO and CO\(_2\) is small for most monitoring situations and does not necessitate applying a correction to measurements.
obtained with the method. Potential interference from sulfur dioxide (SO$_2$) is eliminated by converting any SO$_2$ to sulfate with hydrogen peroxide during analysis (Christie et al, 1970).

**Sample Preservation-**

Collected samples are stable for at least six weeks at room temperature. Stored samples should be tightly sealed to prevent absorption of NO$_2$ from the atmosphere.

**Apparatus**

a. **Sampling** - A diagram of the sampling system is shown in Figure 1.

b. **Sample Inlet** - Teflon$^R$ or glass tube with an inverted Teflon$^R$ or glass funnel at the sampling point to prevent entrance of precipitation.

c. **Absorber** - Polypropylene tube, 164 mm long x 32 mm diameter, equipped with a polypropylene two-port closure (see Figure 1). (Rubber stoppers cause high and variable blank values and should not be used). The closure must be fitted with an 8 mm Outer Diameter of 6 mm Inner Diameter of glass approximately 152 mm long having the end drawn out to form an orifice with an Inner Diameter of 0.3-0.8 mm. This tube must be positioning to allow a clearance of 5 mm from the orifice to the bottom of the absorber. The closure and ports must be free of leaks.

d. **Moisture Trap** - Polypropylene tube similar to absorber. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool or silica gel to trap moisture to protect the flow control device. The trap must be repacked with fresh glass wool or silica gel before the start of each sampling period.

e. **Membrane Filter** - Of 0.8 to 2.0 micron porosity and 3 cm diameter. Be sure the filter does not leak. The filter must be replaced after collecting 10 samples.

f. **Flow Control Device** - Any device capable of maintaining a constant flow through the sampling solution between 180 and 220 cm$^3$/min. A convenient flow control device is a 27 gauge hypodermic needle 10 mm (3/8 in.) long, used as a critical orifice. (Most 27 gauge needles will give flow rates in this range).

g. **Air Pump** - Capable of maintaining a vacuum of at least 0.6 atmospheres (450 torr) across the flow control device. [This value is based on the critical pressure differential, 0.53 atmosphere (400 torr), plus a safety factor to allow for variations in atmospheric pressure and minor variations in pump performance] (Margeson et al, 1977)

h. **Flow meter** - Properly calibrated flow meter for measuring air flow rates in the range of 150-750 cm$^3$/min. The use of a mass flow meter is particularly convenient since no
corrections are required when used under temperature and pressure conditions that differ from the conditions under which it is calibrated.

**Figure 4: NO₂ Sampling Train**

i. Flow Measurement Standard - Precision wet test meter (1 litre/revolution), bubble flow meter, or other reliable standard.

j. Volumetric Flasks - 100, 250, 500, 1,000 ml.

k. Pipets - 1, 2, 5, 10, 15, 20, 50 ml volumetric, 2 ml, graduated in 1/10 ml intervals.

l. Test Tubes - Approximately 150 mm long x 20 mm diameter.

m. Spectrophotometer - Capable of measuring absorbance at 540 nm; equipped with 1 cm optical path length cells.

**Reagents**

All reagents should conform to ACS (American Chemical Society) specifications for reagent grade materials unless otherwise specified.

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

b. Sodium Hydroxide.

c. Sodium Arsenite - CAUTION: Arsenic compounds are highly toxic and should be handled with extreme care. Avoid contact with skin and especially with eyes. Avoid generating dust or breathing dust. Keep away from food. Wash hands after handling it. Do
d. **Absorbing Reagents** - Dissolve 4.0 g of sodium hydroxide in distilled water, add 1.0 g of sodium Arsenite, and dilute to 1,000 ml with distilled water.

e. **Sulfanilamide** - Melting point 165 to 167°C.

f. 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.

g. **Hydrogen Peroxide, 30%**.

h. **Phosphoric Acid, 85%**.

i. **Sulfanilamide Solution** - Dissolve 20 g of sulfanilamide in 700 ml of distilled water. Add, with mixing, 50 ml of 85% phosphoric acid and dilute to 1,000 ml. This solution is stable for one month, if refrigerated.

j. **NEDA Solution** - Dissolve 0.5 g of NEDA in 500 ml of distilled water. This solution is stable for one month, if refrigerated and protected from light.

k. **Hydrogen Peroxide Solution** - Dilute 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 for Preparation of Calibration Graph**

a. **Sodium Nitrite** - Assay of 97% NaNO₂ or greater.

b. **Sodium Nitrite Stock Solution (1000 μg NO₂/ml)** - Dissolve 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:

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

Where, \(G\) = Amount of NaNO₂ in 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.

c. **Sodium Nitrite Working Standard (1.0 μg NO₂/ml)**

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

e. **Solution B** - Pipet 25 ml of solution A into a 250 volumetric flask and dilute to volume with absorbing solution. This contains 1 μg NO₂/ml. Prepare fresh daily.
f. Flow meter - Calibrate the flow meter 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).

g. Absorber - Calibrate the polypropylene absorber by pipetting 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.

h. Spectrophotometer- Prepare calibration curve using 1 μg/ml working standards. 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). Plot absorbance (y-axis) versus the corresponding concentration in μg NO₂/50ml final solution (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve.

Sample Collection

4-Hourly Sampling-
Assemble the sampling apparatus (Figure 4) 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. Add exactly 30 ml of absorbing reagent to the calibrated absorber. Disconnect the funnel, connect the calibrated flow meter, measure the flow rate before sampling and record as F₁. If, the flow rate before sampling is not 1 Lpm, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate of 1 Lpm. Sample for 4 hrs. Record the exact sampling time in minutes as t₁. Measure the flow rate after the sampling period and record as F₂. Seal the collected samples and transport to the laboratory for analysis.

24-Hourly Sampling-
Assemble the sampling apparatus (Figure 4) 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 Tygon®, Teflon®, or polypropylene. Add exactly 30 ml of absorbing reagent to the calibrated absorber. Disconnect the funnel, connect the calibrated flow meter, measure the flow rate before sampling and record as F₁. If, the flow rate before sampling is not between 180 and 220 cm³/min, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24 hrs. Record the exact sampling time, in minutes, as t₁. Measure the flow rate after the sampling period and record as F₂. Seal the collected samples and transport to the laboratory for analysis.
Analysis

Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorber. Mix thoroughly. Pipet 10 ml of the collected sample into a test tube. Pipet 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 reanalyzed as a part of an internal quality assurance program. The overall average efficiency is 82% from 40 to 750 μg NO₂/m³ (0.02 to 0.4 ppm).

Calculation

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

\[ V = \frac{F_1 + F_f}{2} \times t_s \times 10^6 \]

Where, \( V \) = Volume of air sample in m³; \( F_1 \) and \( F_f \) are Air flow rates before and after sampling respectively, in cm³/min; \( t_s \) = Sampling time in minutes; \( 10^6 \) = Conversion of cm³ to m³.

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 flow meter 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 flow meter 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:
\[
\mu g/NO_2^- \times V_s \\
\mu g NO_2/m^3 = \frac{\mu g NO_2/m^3}{V_a \times 0.82 \times V_t} \times D
\]

Where, \(\mu g/NO_2^-\) is NO\(_2\) concentration in analyzed sample; \(V_s\) = Volume of air sample in m\(^3\); 0.82 = Sampling efficiency; \(D\) = Dilution factor (\(D = 1\) for no dilution; \(D = 2\) for 1:1 dilution); \(V_s\) = Final volume of sampling solution; \(V_t\) = Aliquot taken for analysis.

The NO\(_2\) concentration may be calculated as ppm using:

\[
Ppm NO_2 = (\mu g NO_2/m^3) \times 5.32 \times 10^4
\]

2.3. Method for the determination of Sulphur dioxide in air using the modified West and Gaeke method.

Principle

Sulphur dioxide from air is absorbed in a solution of potassium tetrachloro-mercurate (TCM). A dichlorosulphitomercurate complex, which resists oxidation by the oxygen in the air, is formed (West and Gaeke, 1956; Ephraims, 1948). Once formed, this complex is stable to strong oxidants such as ozone and oxides of nitrogen and therefore, the absorber 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 (Lyles et al, 1965). The absorbance of the solution is measured by means of a suitable spectrophotometer. Concentration of sulphur dioxide in the range of 25-1050 \(\mu g/m^3\) can be measured under the conditions given are measured concentration below 25 \(\mu g/m^3\) 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. Beer's law is followed through the working range from 0.03 to 1.0 absorbanse unit. This corresponds to 0.8-27 \(\mu g\) of sulfite ion in 25 ml of final solution calculated as sulphur dioxide. The lower limit of detection of Sulphur dioxide in 10 ml absorbing reagent is 0.75 \(\mu g\) based on twice the standard deviation, which represent a concentration of 25\(\mu g/m^3\) in an air sample of 30 litres.

The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by Sulphamic acid (West and Ordozeva, 1962; Scaringelli et al, 1967; Pate et al, 1965). Ozone is made to decompose by allowing the solution to stand for some time prior to analysis (Zurlo and Griffini, 1962). The interference of trace metals may be eliminated by the addition of Ethylene Di-amine Tetra Acetic Acid
(EDTA) to the absorbing solution prior to sampling (Scaringelli et al, 1967; Zurlo and Griffini, 1962). At least 60 µg iron (III), 10 µg manganese (II), and 10 µg Chromium (III) in 10 ml absorbing reagent can be tolerated in the procedure. No significant interference was found from 10 µg Copper (II) and 22 µg Vanadium (V). Ammonium, Sulphide, and aldehydes do not interfere.

Apparatus

a. Absorber - An all-glass midget impinger, as shown in Figure 5 is recommended for 30 minutes, 1 hour and 4 hours samples. For 24 hours sampling, assemble an absorber from the following parts.

b. Polypropylene Two-Port Tube Closures

c. Glass Impingers - Tubing, 6 cm Outer Diameter and 1.5 cm long. One end is drawn to small diameter so that a No 79 jeweller’s drill bit will pass through, but a No 78 jeweller’s bit will not. The other end is fire polished.

d. Polypropylene Tubes - Tubes 164 by 32 mm, 'Nalgene' or equivalent.

e. Pump - Capable of maintaining an air pressure differential greater than 0.7 atmosphere at the desired flow rate.
f. Air Flow meter or Critical Orifice - A calibrated rotometer or critical orifice capable of measuring air flow within 2%. For 30 minutes sampling, a 22 gauge hypodermic needle 2.5 cm long may be used as a critical orifice to give a flow of about 1 litre/minute. For 1 hour sampling, a 23 gauge hypodermic needle 1.6 cm long may be used to give a flow of 0.2 litre/minute. Use a membrane filter to protect the orifice (Figure 6).

![Figure 6: Central Orifice Flow Control](image)

Analysis

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

\[ A = 2 \cdot \log_{10} T \]

Reagents

a. Water - High quality water must be 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.

b. 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.

CAUTION: HIGHLY POISONOUS IF SPILLED ON SKIN, FLUSH OFF WITH WATER IMMEDIATELY.

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 (Scaringelli et al, 1970). The absorbing reagent is normally stable for six months. If, a precipitate forms, a membrane filter can be used. It may also be necessary after recovering the mercury.
c. **Sulphamic Acid (0.6%)** - Dissolve 0.6 g sulphamic acid in 100 ml distilled water. Prepare fresh daily.

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

e. **Stock Iodine Solution (0.1 N)** - Place 12.7 g iodine in a 250 ml beaker, add 40 g potassium iodide and 25 ml water. Stir until all is dissolved, then dilute to 1 litre with distilled water.

f. **Iodine Solution (0.01 N)** - Prepare approximately 0.01 N iodine solution by diluting 50 ml of stock solution to 500 ml with distilled water.

g. **Starch Indicator Solution** - Triturate 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-stoppered bottle.

h. **Stock Sodium Thiosulfate Solution (0.1 N)** - Prepare 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. Add 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. Add 5 ml starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution.

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

j. **Standardized Sulphite Solution for Preparation of Working Sulphite-TCM Solution** - Dissolve 0.30 g sodium metabisulphite (Na₂S₂O₅) or 0.40 g sodium sulphite (Na₂SO₃) 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 standard sodium thiosulfate solution. To back-titrate, measure, by pipette, 50 ml of the 0.01 N iodine solution 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 reaction 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 0.01N
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.

k. **Working Sulphite-TCM Solution** - Measure 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 sulphur dioxide in the working solution in micrograms of sulphur 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.

l. **Purified Pararosaniline Stock Solution (0.2% Nominal)**

m. **Dye Specifications** - The pararosaniline dye must meet the following specifications:
   (i) 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.
   (ii) 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.
   (iii) 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.

n. **Pararosaniline Stock Solution** - Dissolve 0.500 gm of specially purified pararosaniline (PRA) in 100 ml of distilled water and keep for 2 days (48 hours).

o. **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.

**Sampling**

Procedures are described for short-term (30 minutes, 1 hour, 4 hours long-term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the range in question.

**30 Minutes, 1 Hour and 4 Hours Sampling** - Insert a midget impinger into the sampling system (Figure 5). 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, as shown in Figure 5, or a critical orifice, as shown in Figure 6, 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.

24 Hours Sampling - Place 50 ml TCM solution in a large absorber and collect the sample at 0.2 litre/minute for 24 hours. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Determine the total air volume by multiplying the air flow rate by the time in minutes. The correction of 24 hours measurements for temperature and pressure may be difficult and is not ordinarily done. However, the accuracy of the measurement will be improved if meaningful corrections can be applied if storage is necessary; refrigerate at 5°C. During hot weather, sampling is not recommended unless it is possible to refrigerate the samples as taken. After collection, if a precipitate is observed in the sample, remove it by centrifugation.

For 30 Minutes, 1 Hour and 4 Hours Samples, transfer the sample quantitatively to a 25 ml volumetric flask using about 5 ml distilled water for rinsing. Delay analyses for 20 minutes to allow any ozone to decompose. For 24 Hours Samples, make-up the entire sample to 50 ml with absorbing solution. Measure 5 ml of the sample into a 25 ml volumetric flask by pipette for chemical analysis. Bring volume to 10 ml with absorbing reagent. Delay analysis for 20 minutes to allow any ozone to decompose.

Sample Preservation - After sample collection, the solutions must be stored at 5°C in a refrigerator. At 22°C, losses of sulphur dioxide occur at the rate of 1% per day. When samples are stored at 5°C for 30 days, no detectable losses of sulphur dioxide occur. The presence of EDTA enhances the stability of sulphur dioxide in solution, and the rate of decay is independent of the concentration of sulphur dioxide (Scaringelli et al, 1967).

Determination

For each set of determinations prepare a reagent blank by adding 10 ml of unexposed TCM solution to a 25 ml volumetric flask. Prepare 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 the sample, control solution or reagent blank, add 1 ml 0.6%
sulphamic acid and allow it to react for 10 minutes to destroy the nitrite resulting from oxides of nitrogen. Measure by pipette and add 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**

a. **Flow meter and Hypodermic Needle** - Calibrate flow meter and hypodermic needle (Lodge et al, 1966) against a calibrated wet test meter.

b. **Calibration Curve - Procedure with Sulphite Solution** - Measure 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. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents. 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. Plot the absorbance against the total concentration in micrograms sulphur dioxide for the corresponding solution. The total micrograms sulphur
dioxide in solution equals the concentration of the standard in micrograms sulphur 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. 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.

c. **Sampling Efficiency** - Collection efficiency is generally above 98%; efficiency may fall off, however, at concentrations below 25µg/m³ (Urone et al, 1965 and Bostrom, 1965).

**Calculation**

**a. Normality of Thiosulphate 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 in ml; W - Weight of potassium iodate (grams); 35.67 - Equivalent weight of potassium iodate.

**b. Concentration of Sulphite Solution**

The amount of sulphur dioxide per milliliter in the standard solution is calculated as follows:

\[ C = \frac{(V₁ - V₂) \times N \times K}{V} \]

Where, C - SO₂ concentration in µg/ml; V₁ - Volume of thiosulfate for blank in ml; V₂ - Volume of thiosulfate for sample in ml; N - Normality of thiosulfate; K - 32000 (Milli equivalent weight SO₂/µg), V - Volume of standard sulphite solution in ml.

**c. Conversion of Volume**

Convert the volume of air sampled to the volume at the reference conditions of 25°C and 760 mm:
P 298

\[ V_r = \frac{V \times \frac{(t + 273)}{760} \times \frac{10^3}{1}} \]

Where, \( V_r \) - Volume of air at 25°C and 760 mm Hg in litres; \( V \) - Volume of air sampled in litres; \( P \) - Barometric pressure, mm Hg; \( t \) - Temperature of air sampled in °C.

d. **Sulphur Dioxide Concentration at the Reference Conditions**

When sulphite solutions are used to prepare calibration curves, compute the concentration of sulphur dioxide, \( C \), in micrograms per cubic metre, in the sample as follows:

\[ (A - A_o) (10^3) (B) \]

\[ C = \frac{\text{Conversion factor, } \mu g/\text{absorbance unit}}{V} \]

Where, \( A \) is Sample absorbance; \( A_o \) - Reagent blank absorbance; \( 10^3 \) - Conversion of litres to cubic metres; \( V_r \) - Volume of air corrected to 25°C and 760 mm Hg in litres; \( B \) - Calibration factor, \( \mu g/\text{absorbance unit} \); \( D \) - Dilution factor

e. **The Concentration of SO\textsubscript{2} in \( \mu g/m^3 \) in the sample is calculated as follows:**

\[ (A - A_o) \times 10^3 \times B \]

\[ C (SO_2 \mu g/m^3) = \frac{\text{Conversion of Micrograms per Cubic Metre to Parts per Million}}{V} \]

Where, \( A \) - Sample absorbance; \( A_o \) - Reagent blank absorbance; \( 10^3 \) - Conversion litres to cubic meters; \( B \) - Calibration factor, \( \mu g/\text{absorbance} \); \( V \) - Volume of air sampled in liters

f. **Conversion of Micrograms per Cubic Metre to Parts per Million**

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

\[ \text{Ppm SO}_2 = \mu g \text{SO}_2/m^3 \times 3.82 \times 10^4 \]

**Precision and Accuracy** - Relative standard deviation at the 95% accuracy level is 4.6% for the analytical procedure using standard samples (Pate et al, 1965)

### 2.4 Method for measurement of Respirable Suspended Particulate Matter (PM\textsubscript{10}) in Ambient Air (Cyclonic Flow Technique).

The purpose is to lay down a uniform and reliable method for determination of PM\textsubscript{10} (Particulate matter less than 10\( \mu \)m diameter) in ambient air.
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. 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 PM$_{10}$ in the designated size range is calculated by dividing the weight gain of the filter by the volume of air sampled (Intersociety committee, 1966).

Other Analysis – Depending on the type of filter media used, filter samples can be analyzed for lead, iron, organic and elemental carbon, extractable organic material, elements, radioactive materials, inorganic compounds, and single particles.

Range and Sensitivity
a. Lower Quantifiable Limit – For 24-h sample duration at 1132 L/min, the detection limit is determined by the reproducibility of the filter weight difference which shows a standard deviation (sigma) of approximately ± 2mg. The three-sigma detection limit is 3.5μg/m$^3$ approximately. The three-sigma lower quantifiable limit depends on the filter used and may be as high as 5 μg/m$^3$.

b. Upper Quantifiable Limit – For 24-h sample duration at 1132 L/min, this limit is in the range of 400 to 1000μg/m$^3$. The exact value depends on the nature of the aerosol being sampled: very small particles will clog the filter at a relatively low mass loading while larger particles will fall off during sample transport at high concentrations.

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

d. Re-circulation- Re-circulation 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 0.15 μg / m$^3$ 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 blower exhaust away from the sampler.

e. 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 SO$_2$ concentrations have been shown to yield up to 10 μg/m$^3$ 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, flow rate through the filter, and sampling time have 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 with independent standards. These uncertainties combine to yield a propagated precision of approximately ± 13% at 10 μg/m³ and approximately ± 5% at 100μg/m³. The filter deposit mass measurement precision dominates at low concentrations while the flow rate precision dominates at high concentrations.

Apparatus

a. Sampler - The essential features of a typical high volume sampler are shown in figure-1. It is a compact unit consisting a protective housing, blower, voltage stabilizer, time totalizer, rotameter and filter holder.

b. Inlet for PM₁₀ sampling

c. Cyclonic Flow Inlet - 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 air stream. In a typical cyclone pre-collector, the air enters tangentially at its side and swirls around inside. Particles above μm are thrown to the cyclone walls and collected at its base ("grit-pot"). The air containing the respirable dust leaves through the central exit at the top of the cyclone and is filtered to collect the dust on a filter paper.

d. 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 for the resistance of the filter being used. The flow rate decreased as filter deposit increases, but this change is normally less than 10% and is quantifiable via pre- and post-exposure flow measurements.

e. Laboratory Equipment

1. **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 and relative humidity of 20 to 45% with ± 5% variability is recommended.

2. **Analytical Balance** – The balance must be equipped with an expanded weighing chamber to accommodate 20.3 x 25.4 cm (8x10 in.) filters and must have a sensitivity of 0.1 mg.

3. **Equilibration Rack** – This rack separates filters from one another so that the equilibration air can reach all parts of the filter surface. A photograph record rack serves this purpose well.

4. **Numbering Machine** – Though filter ID numbers can be written on the edge of filters with a pen, an incrementing numbering machine that print 4 to 8 digit ID numbers is more efficient and is less likely to damage the filter.

5. **Wet Bulb/Dry Bulb Psychrometer** – 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.

f. Calibration and Auditing Equipment

1. **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.

2. **Orifice Transfer Standard** – The PM10 sampler calibration orifice consists of a 3.175 cm (1.25 in) 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 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 pressure difference and flow rate is established via a calibration curve derived from measurements against a primary standard 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 circulated discs.

3. **Manometer** – A calibrated pressure gauge or water manometer spanning 0 to 15 inches of water (0-4 k Pa) is used to determine the pressure drop across the orifice.

4. **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 k Pa (4% of standard 101.3 k Pa).

5. **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).

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

7. **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. At each weighing session, a balance calibration check is performed using a Class S or Class M weight.

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**Reagents**

a. **Filter Media** – A 20.3 x 25.4 cm (8 x 10 in) glass fibre 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. United States Environmental Protection Agency (USEPA) filter requirements specify 0.3 μm DOP sampling efficiency in excess of 99%, weight losses or gains are due to mechanical or chemical instability of less than a 5 μg/m³ equivalent, and alkalinity of less than 25 micro-equivalent /gram to minimize sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) absorption. The most appropriate filter media for high volume sampling are cellulose fibre, glass fibre, quartz fibre, Teflon coated glass fibre and Teflon membrane. None of these materials is perfect for all purposes.

Glass fibre filters meet requirements in most categories with the exception of artifact formation and blank levels. Sampling efficiency is very high for all particle sizes. Blank
levels for several elements of interest are high and variable. Glass fibre filters may exhibit organic carbon artifacts.

b. **Filter Jacket** — A smooth heavy paper folder or envelop 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**

a. **Filter Inspection** — Clean the light table surface with a methanol soaked wiper and allow it to dry. Filters should be handled with gloved 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.

b. **Filter Identification** — Apply an ID number to the upper right hand corner on the smoother 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 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.

c. **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.

d. **Filter weighing** — It is best to weight 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, 00,000 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 can not 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-weigh them and subtract this check-weight value from the corresponding routine weigh. 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.

e. **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 necessary to read just 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 wing 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 manually 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 its 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 reading (hourly) of the 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 length wise 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.

Calculation

Calculation of volume of air sampled

\[ V = QT \]

Where, \( V \) = Volume air sampled in m\(^3\); \( Q \) = Average flow rate in m\(^3\)/minute; \( T \) = Total sampling time in minute

Calculation of PM\(_{10}\) in Ambient Air

\[ \text{PM}_{10} = \frac{(W_f - W_i) \times 10^6}{V} \]

Where, \( \text{PM}_{10} \) = Mass concentration of particulate matter less than 10 Micron Diameter in \( \mu \text{g}/\text{m}^3 \); \( W_i \) and \( W_f \) are initial and final weights of filter in grams; \( V \) = Volume of air sampled in m\(^3\); \( 10^6 \) = Conversion of g to \( \mu \text{g} \)

2.5 Determination of CO Concentration in Ambient Air

The Indicator Tube method (http://www.who.int/ipcs/publications/ehc/ehc_213_part_2.pdf) was engaged to measure the CO concentration. The analyzer utilizes ambient air, which is filtered through catalyst located inside the instrument as reference gas in order to measure the concentration of CO. The pollutants from the ambient air are sucked through a glass sampling tube at a height of about 4m above the ground surface. This process uses an indicator tube containing potassium palladousulphite in which air is passed over an adsorbent until equilibrium is established between the concentration of carbon monoxide in the air and the concentration of carbon monoxide on the adsorbent. This simple and inexpensive measurement technique uses detector tubes (indicator tubes) and is based on the reaction:

\[ 5\text{CO} + I_2\text{O}_4 \rightarrow I_2 + 5\text{CO}_2 \]

The iodine-coloured layer in the tube corresponds in length to the carbon monoxide concentration in the sample.
2.6. Ambient Noise Quality Experiment

Ambient noise quality monitoring in the six different residential areas was executed using the Lutron digital sound level meter, model: SL-4001 (Figure 2). It is a small and light-weight variant and has dimensions of 205 x 80 x 35 mm (8.1 x 3.2 x 1.4 inch) with a total range of 30 dB to 130 dB. The measurement can be carried out in three different sub-ranges of 30 dB to 80 dB, 50 dB to 100 dB and 80 dB to 130 dB, with 50 dB interval on each step. The resolution of the instrument is 0.1 dB. Fast time weighting of $t = 200$ milli seconds (ms) is chosen to simulate the human ear response time weighting, whereas slow-time weighting of $t = 500$ ms is used to obtain the average values of vibrational sound level, which is not applicable here.

Hence, the ‘A’ standard frequency weighting network must be employed because it’s character has been simulated as ‘human ear listing’ response. For this particular reason, ‘A’ weighting must be used for all environmental sound level measurements. ‘C’ standard weighting is widely used when the characteristic is near the ‘FLAT’ response in case of checking the noise levels emitted from machinery for quality control (QC) check and for determining the sound pressure level of the tested equipment, which does not suit the present context of the study.

The frequency range that can be covered with this sound meter is 31.5 Hz – 8,000 Hz. The frequency weighting on this device meets the International Electro Technical Commission (IEC) 651, type 2 specifications. The input signal is calibrated on 94 dB (in the frequency range 31.5 Hz to 8 kHz).

A ½-inch standard size electret condenser microphone is used to transduce the acoustic signals into electric signals. The Bruel and Kjaer multi-function acoustic calibrator, model 4226 is used as it enables simulated free-field calibration of microphones, sound level meters and other related instruments. Type 4226 generates accurate and stable sound pressure with a frequency varying from 31.5 Hz to 16 kHz in octave steps, plus a signal at 12.5 kHz. Using the coupler provided, the test signal can be applied to either ½-inch or ¼-inch microphones, or picked up from an electrical output. For ease of use, type 4226 can also apply a very accurate inverse A-weighting correction.
The instrument can be calibrated externally using a screwdriver, provided along with
the meter. It consists of an internal oscillation system that generates a 1 kHz sine
wave. The operating temperature of this sound meter is 0°C to 50°C (32°F to 122°F)
and this functions effectively with optimum reliability as long as the relative humidity
of the ambient air does not exceed 80%.

For many types of noise, it has been found in practice that a simple measurement of
dB(A) using a sound level meter correlates the best with the more complicated
approach of noise level estimation from a frequency analysis. For this reason, dB(A)
measurements are widely used in reporting noise measurements.

The origin of the word ‘Bel’ can be traced back to the 1920s when it was coined in
honour of Alexander Graham Bell to describe attenuation in telephone cables. One Bel
is the ratio R, given by:

\[ \log_{10} R = 1 \]

Hence, \( R = 10 \)

For convenience of calculation, a smaller ratio, decibel is commonly used. One decibel is the
ratio ‘r’ given by:

\[ \log_{10} r = 0.1 \]

Hence \( r = 1.26 \)

The intensity of sound is proportional to the amount of sound energy received per
second from the source of sound. The level of intensity is ten times the logarithm of
intensity ratio, which is given as:

\[ I_L = 10 \log (I/I_0) \]

Where, \( I_L \) = Intensity level; \( I \) = Measured intensity; \( I_0 \) = Reference intensity

Also, intensity is directly proportional to the square of pressure. Hence,

\[ I_L = (P)^2 = 2 \times 10 \log (P/P_0) = 20 \log (P/P_0) = \text{Sound Pressure Level (SPL)} \]

So, there are some practical difficulties in measuring the intensity. But the variation in
pressure can be easily measured. As intensity exhibits a direct relation with pressure
(Square of pressure), the sound pressure level in decibel is given by:

\[ \text{SPL} = 20 \log (P/P_0) \text{ dB} \]

Here, \( P_0 \) is the reference pressure, which has a value \( 2 \times 10^5 \text{ Nm}^{-2} \) and \( P \) is the
measured pressure in Nm\(^{-2}\). This value of \( P_0 \) is used extensively as it has been
evaluated to be the nearest whole number that corresponds to the reference intensity.
Equivalent Average Sound Level $L_{eq}$:

Noise evaluation is often carried out over an extended period, during which the noise level can vary between wide limits. The equivalent sound level $L_{eq}$ is defined by:

$$L_{eq} = 10 \log \frac{1}{T} \int_{t_1}^{t_2} \left( p(t) \right)^2 dt$$

Where, $T = t_2 - t_1$ is the measurement time.

$L_{eq}$ is the constant sound level which would give the listener the same "noise dose" (of sound energy) as the actual sound over the measurement time. Frequently the time-varying sound pressure $p(t)$ is filtered in accordance with the A-weighting curve. The arithmetic mean of 'n' sound levels (say, $L_1$, $L_2$, $L_3$, ..., $L_n$) given by:

$$L_{\text{Mean}} = \frac{1}{n} \left[ L_1 + L_2 + L_3 + ... + L_n \right]$$

Further, the energy average, also called 'effective' or 'rms' of these 'n' sound levels is given by the relation:

$$L_{eq} = 10 \log_{10} \left\{ \frac{1}{n} \left[ 10^{L_1/10} + 10^{L_2/10} + 10^{L_3/10} + ... + 10^{L_n/10} \right] \right\}$$

A continuous record of Sound Level Meter (SLM) against time is used for storage. The noise average meter is fed directly or from magnetic tape recording to give $L_{eq}$. $L_{eq}$ is the equivalent continuous sound pressure level with certain limitations, capable of causing the same effect. Finally, noise analyser data is fed directly to the sound level meter. The sound signal is converted into electrical signal by a high quality microphone. Then, the signal is amplified to display the noise level reading on decibel (dB) scale. For this, the microphone has to possess Omni-directional sensitivity (sensitive in all directions).

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