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COMPREHENSIVE INDUSTRY DOCUMENT
SERIES : COINDS/20/1984-85

EMISSION REGULATIONS

PART - THREE

CENTRAL POLLUTION CONTROL BOARD

July, 1996

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PART - THREE

CENTRAL POLLUTION CONTROL BOARD
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PREFACE

As an integral part of the emission regulations, it is necessary to have standard methods of sampling and analysis of air pollutants. The standards for stack emissions were evolved in July 1984 (Part I) and July 1985 (Part II). The monitoring requirements are a sequel to these.

N Chaudhuri

(NILAY CHAUDHURI)
Chairman

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CHAPTER-1

1.0.0 Monitoring Requirements for Industries

The industrial units are required to monitor ambient air quality and stack emission within industrial premises. The exact location of ambient air quality monitoring stations and the sampling ports in the stacks shall be decided by the concerned industrial units in consultation with the relevant State Pollution Control Board.

The new industrial units shall have sampling ports built into the stack as per Figure 2.5. A permanent sampling platform and approach shall also be provided to the stack sampling station, as given in the section entitled 'Sampling Port', under 2.5.0.

The State Board may prescribe more rigorous monitoring requirements depending on the location of the industry and specially if it is in a protected area.

1.0.1 Certification

1.0.2 All monitoring equipment and instrument shall be of standard design approved by the Central Pollution Control Board or an agency like State Pollution Control Board as delegated by Central Pollution Control Board.

1.0.3 The agency or laboratory performing the monitoring of stack emission and ambient air quality tests shall have to be approved by the State Pollution Control Board in consultation with Central Pollution Control Board. In a case where a dispute occurs, this will be resolved by the tests being conducted by the Central Pollution Control Board or its approved laboratory.

1.1.0 General Requirements

1.1.1 Stack monitoring shall be done following the frequency given for each industry. The report shall be sent to the concerned State Board in a standardized format. Table 3.1 is cited as an example taking particulatematter as the pollutant.

1.1.2 In case there is more than one equipment connected to a single stack then the emission from each equipment must be individually reported. In this case the sampling ports may be made in the duct and not in the stack.

1.1.3 The parameters for stack monitoring, in addition to pollutant(s), must include the air flow rate (Nm^3/hr) and the production during period of sampling.

1.1.4 Ambient air quality sampling shall be done on a 24 hour basis every alternate day. The report for each month shall be sent to the concerned State Board in the format of Table 6.1.

1.1.5 The parameters for monitoring, in addition to pollutant(s), shall include micrometeorological data of wind speed and direction and the wet and dry bulb temperatures. In cases where there is more than one ambient air quality station, the wind and temperature data may be obtained from only one station.

1.1.6 In cases where there are a number of contiguous industries, the State Board would decide on the deviation from the required number of ambient monitoring stations.

1.2.0 The maintenance and operation of the required number of ambient monitoring stations and the frequency of source emission monitoring shall be as follows. The stations are to be set up at the boundary of the manufacturing or processing facility.

1.2.1 Cement

Plant Capacity TPA	Ambient Air Quality Monitoring Stations	Source Emission Monitoring
Less than 100,000 and including mini cement plant	Not required	Once in 8 weeks
100,000 upto 300,000	2 Stations	Once in 4 weeks
300,000 upto 600,000	3 Stations	Once in 2 weeks
600,000 and above	4 Stations	Once in a week

The parameter to be monitored shall be suspended particulate matter in ambient air and total particulates in the stack.

1.2.2 Thermal Power

Boiler Capacity MW	Ambient Air Quality Monitoring Stations	Source Emission Monitoring
Less than 200	2 Stations	Once in 4 weeks
Greater than and including 200	3 Stations	Once in 2 weeks
Greater than and including 500	4 Stations	Once in 1 week

The parameters to be monitored shall be suspended particulate matter, sulphur dioxide and nitrogen dioxide in the ambient air and total particulates and sulphur dioxide in the stack. All stack gas emission results shall be normalized to 12 % CO_2 in the flue gas.

1.2.3 Integrated Iron and Steel

Plant	Source Emission Monitoring
Sintering	Once in 2 weeks
Steel making	Once in 2 weeks

There shall be four ambient air quality monitoring stations for each steel plant. The parameters to be monitored shall be suspended particulate matter, sulphur dioxide and nitrogen dioxide in the ambient air and total particulates in the stack.

1.2.4 Fertilizer

Plant type	Ambient Air Quality Monitoring Stations	Source Emission Monitoring
Phosphatic	Three	Once in 4 weeks
Nitrogenous	Three	Once in 8 weeks
Mixed	Three	Once in 8 weeks

If the same factory has more than one type of plant, then the number of ambient air quality monitoring stations need not increase, only the parameters would.

The parameter to be monitored in phosphatic fertilizer plants shall be suspended particulates and total fluorides in the ambient air and total particulates and total fluorides in the stack. In the case of nitrogenous and mixed fertilizers, suspended particulates shall be monitored in the ambient air and total particulates in the stack.

1.2.5 Nitric Acid

Plant Capacity TPD	Ambient Air Quality Monitoring Stations	Source Emission Monitoring
Less than 150	2 Stations	Once in 4 weeks
Greater than and including 150	3 Stations	Once in 2 weeks

The parameter to be monitored shall be oxides of nitrogen, both in the ambient air and in the stack gases.

1.2.6 Sulphuric Acid

Plant Capacity TPD	Ambient Air Quality Monitoring Stations	Source Emission Monitoring
Less than 100	2 Stations	Once in 4 weeks
Greater than and including 100	3 Stations	Once in 2 weeks

The parameter to be monitored shall be sulphur dioxide both in the ambient air and in the stack gases.

1.2.7 Primary Aluminium

Each facility must have four ambient air quality stations for monitoring suspended particulate matter, sulphur dioxide and total fluorides. The emissions from the cells shall be monitored for total particulates and fluorides every week, while emissions from other stacks shall be monitored once every four weeks.

The stacks from the crusher and alumina drying kiln shall be monitored for total particulates, the boiler stacks for total particulates and sulphur dioxide and the stack for anode baking for sulphur dioxide.

1.2.8 Carbon Black

The emissions from carbon black manufacturing shall be monitored for particulate matter and carbon monoxide once every eight weeks.

1.2.9 Calcium Carbide

Each facility must have three ambient air quality stations for monitoring suspended particulate matter. The emissions from the kiln and arc furnance shall be monitored once every four weeks for particulate matter.

1.2.10 **Oil Refinery**

The emissions from the stacks of distillation unit, catalytic cracker and sulphur recovery unit shall be monitored continuously for sulphur dioxide in the oil refineries in Mathura and in Bombay. The schedule for the other refineries shall be as given below:

Refining Capacity tonnes crude / day	Ambient Air Quality monitoring Stations	Source Emission Monitoring
Less than 3000	3 Stations	Once in 4 weeks
3000 and higher	4 Stations	Once in 2 weeks

Source emission monitoring for stacks other than distillation and catalytic cracker unit shall be done once in 8 weeks for refineries processing less than 3000 TPD of crude and once in 4 weeks for the larger units.

CHAPTER-2

STACK MONITORING-EQUIPMENT AND TESTING PROCEDURE

2.0.0 Source Emission Monitoring

2.1.0 This section deals with the methods of source emission monitoring. It also gives the minimum requirements of a stack monitoring equipment.

2.2.0 Specifications of Stack Monitoring Equipment

2.2.1 General

Stack Velocity Range: 0 to 30 m/sec
Stack Temperature Range: 0 to 600°C
Particulate Sampling: At 10 to 100 lpm
Filter Paper (Thimble): Collection of particulates down to 0.3 micron

Gaseous sampling: At 1 to 2 lpm collection on a set of impingers, containing selective reagents

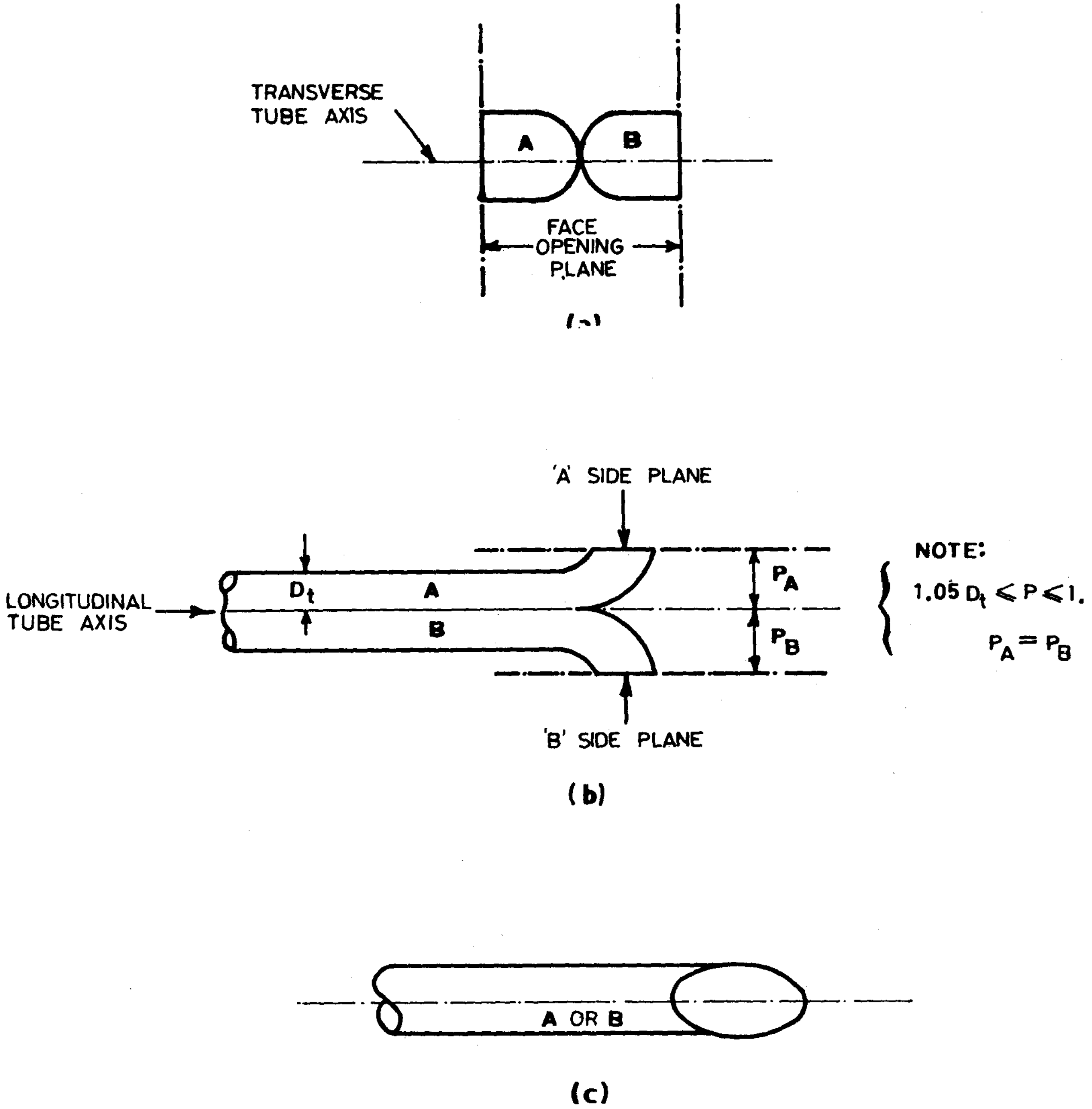
2.2.2 Pitot Tube

i. Modified S-type pitot tube shall be fabricated from SS 304 or equivalent. The construction features should be as per United States Environmental Protection Agency (EPA) regulations, Method 2, given in Figures 2.1 and 2.2.

ii. Standard pitot tube shall be fabricated from SS 304 or equivalent. The construction features shall be such that the coefficient of the pitot tube is above 0.95.

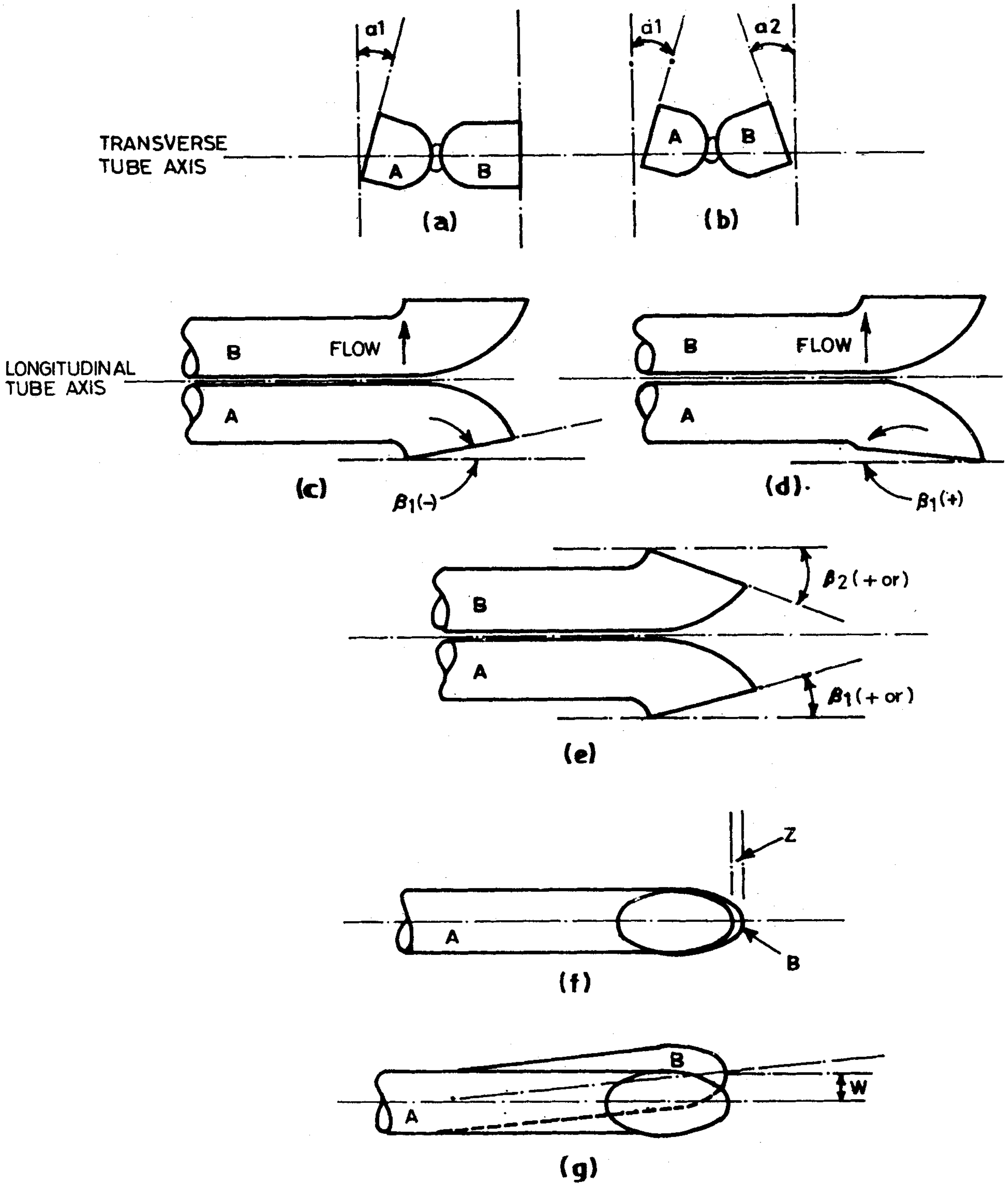
2.2.3 Sampling Probe

Fabricated from SS 304 tube of suitable diameter (not less than 15 mm ID). The lengths of the pitot tube and the sampling probe shall be decided between the user and the manufacturer.



Properly constructed Type S pitot tube shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

FIGURE 2.1 S-TYPE PITOT TUBE CONSTRUCTION



Types of face opening misalignment that can result from field use or improper constructruction of Type S pitot tubes. These will not effect the baseline value of Cp(s) so long as a_1 and $a_2 < 10°$, $\beta_1$and $\beta_2 < 5°$. $z < 0.32$ cm (1/8 in.) and $w < 0.08$cm (1/32 in.)

FIGURE 2.2 S-TYPE PITOT TUBE CONSTRUCTION

2.2.4 Nozzles

A set of nozzles fabricated from SS 304 or equivalent material with internal diameters suitable to cover the full range of stack velocities. The leading edge of the nozzle should be sharp and tapered. The minimum internal diameter of the nozzle should not be less than 8 mm.

2.2.5 Thimble Holder

Filter paper holders fabricated from SS 316 suitable to hold alundum / cellulose / glass fiber / asbestos thimbles.

2.2.6 Thermocouple

Thermocouple sensor with analog or digital dial gauge capable of measuring temperature from 0 to 600°C covered with stainless steel or mild steel casing with acid resistant treatment.

2.2.7 Mounting Flange

A pair of male/female flanges fabricated out of mild steel with proper hole for mounting thermocouple sensor, sampling tube and pitot tube.

2.2.8 Panel Box Sides

Fabricated out of aluminium / mild steel / fiber glass sheets with oven-baked stove-enamel finish. It should have suitable arrangements for housing stop-watch, manometer, rotameter, dry gas meter, etc.

2.2.9 Back Panel

Hinged door panel of mild steel to contain cold box with 6 impingers.

2.2.10 Inclined-cum-Vertical Manometer

Fabricated out of solid acrylic sheets. Inlet and outlet provided at the ends for filling in gauge fluid. Spirit level attached for levelling. Velocity range: 0 to 30 m/sec.

2.2.11 Rotameters

0 to 100 lpm for particulate monitoring and 0 to 3 lpm for gaseous monitoring.

2.2.12 Stop-Watch

0 to 60 minutes, one second readout with hold facility.

2.2.13 Impingers

Four number 100 ml and two number 300 ml capacity. Facility should be there for keeping ice at the bottom of impinger box.

2.2.14 Vacuum Pump

Rotary design, with a capacity of to 0 to 120 lpm gas flow with single phase motor, 220 V. The pump will also have a moisture trap, air inlet valve and mounted inside a pump housing and should be portable.

2.2.15 Dry Gas Meter

The sampling train shall have a dry gas meter with the facility for measuring temperature and static pressure. The capacity of the meter should be adequate to record upto 100 lpm of airflow and a minimum readout of 0.001 cubic meters.

2.2.16 Pump Housing

Mild steel case with oven-baked stove-enamel finish and ON/OFF switch with indicator lights.

2.2.17 Tools

A kit containing the essential tools required for connecting various components shall be provided with the equipment.

2.2.18 Train Leakages

The sampling train after having set up will be tested for leakage by plugging the inlet. The rotameter shall not give a reading beyond 5 lpm when the flow has been set at 100 lpm. Also the dry gas meter should give a reading of less than 5 percent of the air flow.

2.3.0 Method of Testing

2.3.1 Selection of Sampling Site

The objective of sampling is to determine the amount of pollutant being emitted from a stack. This limit will be as per the regulations of the Central and State Boards. The site should be such that a laminar flow of air is present in the stack.

The guidelines for selection are given under 2.4.0 of this chapter.

2.3.2 Traverses

The number of traverses to be made will be as per 2.4.2. All new stacks should have a sampling port and sampling platform, the location of which will be decided by the relevant State Board.

2.3.3 Molecular Weight Determination

This is determined by drawing a known quality of gas into an Orsat Apparatus or a gas chromatograph. Also the moisture should be found. Knowing the gas consituents, the molecular weight is found as given in 3.3.0.

2.3.4 Velocity Determination

The pitot tube is now connected as given in Figure 3.2. The dynamic and a static pressure is found by using the manometer. The temperature inside the duct is also measured. The velocity of gas in the duct and the air quantity are found using the formula given in 3.4.0 and 3.4.1.

2.3.5 Moisture Determination

The moisture content may be determined either by the condensor method or by wet and dry bulb temperature and then referring to a suitable psychrometric chart. Latter should be limited to non-acid gas streams with moisture content of less than 15 percent and dew point less than 52°C. The condensor method works well for most gas streams and is also relatively easy to perform. These methods are given in 3.5.0 and 3.6.0.

2.3.6 Results

All results shall be normalized to 25°C and a pressure of 1.01 kPa (760 mm of mercury) on a dry basis (zero percent moisture).

2.4.0 Selection of Sampling Site and Minimum Number of Traverse Points

Select the sampling site at any cross section of the stack or duct that is at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as bend, expansion, contraction, visible flame, or stack exit (see inset, Figure 2.3). For rectangular cross sections the larger dimension shall be used to represent the stack diameter.

2.4.1 When the above sampling site criteria can be met, determine the minimum number of traverse points required, from Table 2.1. The minimum required number of traverse points is a direct function of stack or duct diameter.

2.4.2 When a sampling site such as described in 2.4.0 is not accessible, choose a convenient sampling location and use Table 2.1 and Figure 2.3 to determine the minimum required number of traverse points. First, measure the distance from the chosen sampling location to the nearest upstream and downstream disturbance. Then, from Figure 2.3 determine the corresponding sample point multiples for both distances and select the greater of these. Multiply it by the number obtained from Table 2.1. The result of this calculation is the minimum number of traverse points required. This number may have to be increased such that for circular stacks the number is a multiple of 4 and for rectangular stacks the number follows the criteria given in 2.4.4.

2.4.3 Cross - Sectional Layout and Location of Traverse Points

For circular stacks divide the cross section into equal parts by two right-angle diameters. Locate half the traverse points symmetrically along each diameter according to Figure 2.4 and Table 2.2.

2.4.4 For rectangular stacks divide the cross section into as many equal rectangular areas as there are traverse points such that the ratio of the length to the width of the elements/area is between one and two. Locate the traverse points at the centroid of each area according to Figure 2.4.

2.4.5 Under no conditions shall a sampling point be selected within 3 cm of the stack wall.

Table 2.1 MINIMUM REQUIRED NUMBER OF TRAVERSE POINTS FOR SAMPLING SITES WHICH MEET SPECIFIED CRITERIA

Inside diameter of stack or duct (m)	Number of points
I.D. $\leq$ 0.3	4
0.3 $\leq$ I.D. $\leq$ 0.6	8
0.6 $\leq$ I.D. $\leq$ 1.2	12
1.2 $\leq$ I.D. $\leq$ 2.4	20
2.4 $\leq$ I.D. $\leq$ 5	32

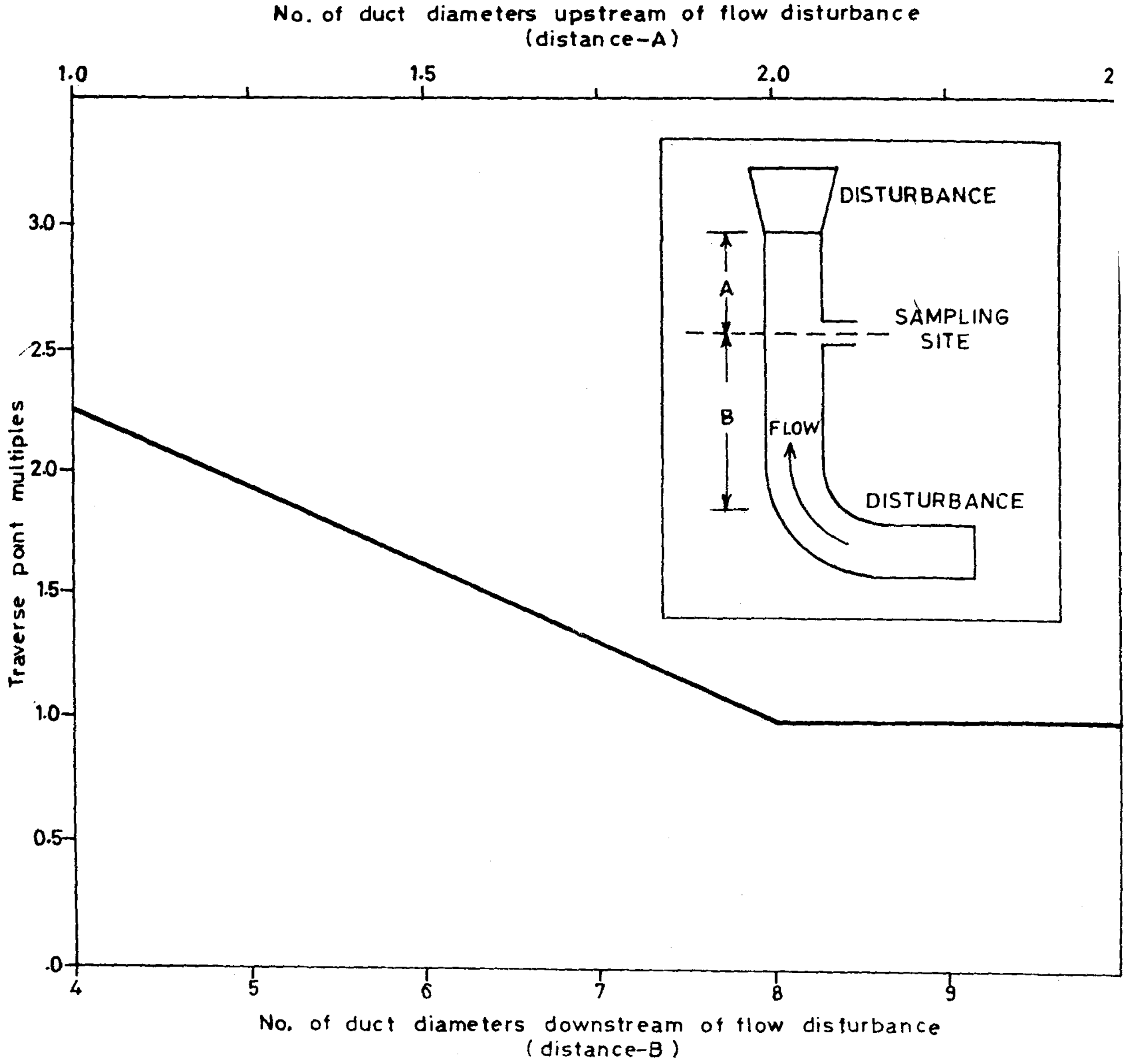


FIGURE 2.3 TRAVERS POINT MULTIPLES TO DETERMINE MINIMUM NUMBER OF TRAVERSE POINTS REQUIRED WHEN A<2 OR B<8

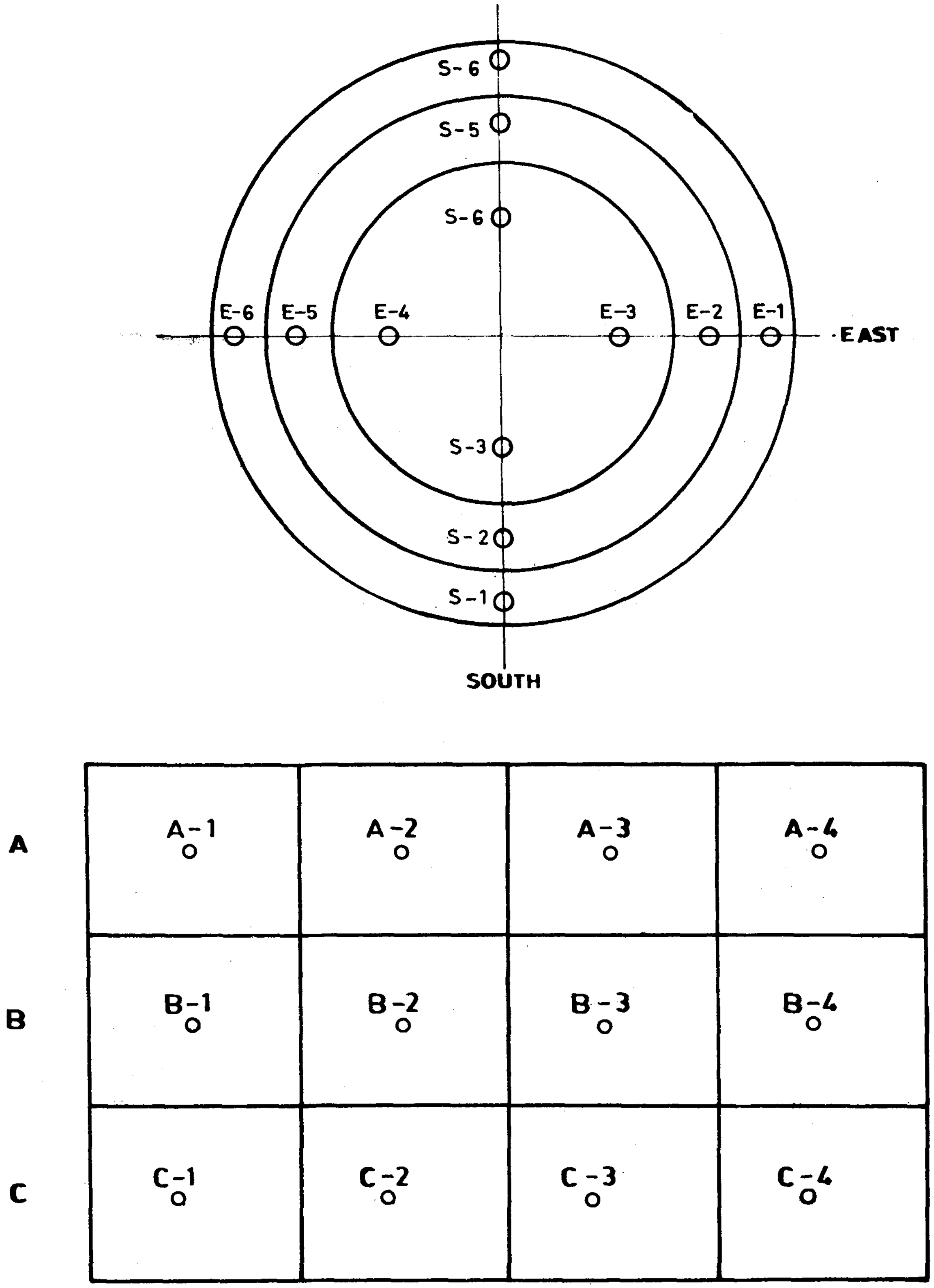


FIGURE 2.4 LOCATION OF TRAVERSE POINTS ON CIRCULAR AND RECTANGULAR CROSS SECTIONS DIVIDED INTO TWELVE EQUAL AREAS

Table 2.2 LOCATION OF TRAVERSE POINTS ON DIAMETERS OF CROSS SECTIONS OF CIRCULAR STACKS

TRAVERSE POINT NUMBER ON A DIAMETER	PERCENT OF STACK DIAMETER FROM INSIDE WALL TO TRAVERSE POINT											
	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

2.5.0 Location of Sampling Port

To ensure laminar flow the sampling ports shall be located at atleast 8 times chimney diameter down stream and 2 times up stream from any flow disturbance. For a rectangular cross section the equivalent diameter (De) shall be calculated from the following equation to determine up stream, down stream distances.

$$De = \frac{2 L W}{L + W}$$

Where L = Length in m, W = width in m.

Sometimes it may so happen for existing chimneys that sufficient physical chimney height is not available for desired sampling location in such cases additional traverse points shall be taken as given under 2.4.0.

The sampling port should be preferably provided on the delivery side of duct or chimney and not on the suction side.

2.5.1 Number of Sampling Port

The pitot tubes commercially available in the country generally do not exceed 2 meters in length. Any point on the horizontal cross-section of a stack (chimney) along any diameter can be measured for flow by the pitot tube, if the point is approachable by the pitot tube inserted through the sampling port (hole). Minimum two (mutually orthogonal) sampling ports are required in a circular chimney so that full stack cross-sectional area can be covered for measurements, so long as the diameter of the stack is less than 2 meters.

The stack having a diameter between 2 and 4 meters, the two mutually orthogonal sampling ports are to be increased to four by having the other two sampling ports at diametrically opposite positions to the first two sampling ports (Figure 2.5).

2.5.2 Dimensions of Sampling Port

Port Type: Pitot tube, temperature and sampling probe are to be inserted together into the sampling port for monitoring purposes. Sampling port should be a standard flanged pipe of 0.10 m inside diameter (ID) with 0.15 m bolt circle diameter. An easily removable blind flange should be provided to close the port when not in use (Figure 2.5).

Port Installation: Flanged pipe used as port should be installed with the interior stack wall. Port should extend outward from the exterior stack wall not less than 50 mm and not more than 200 mm only when additional length is required for gate valve installation. Ports should be installed at a height between 0.90 and 1.2 m above the floor of the working platform.

Port Loading: The port installations should be capable of supporting the following loads:

a. Vertical shear of 91 kg
b. Horizontal shear of 23 kg and
c. Radial tension of 23 kg (along stack diameter)

2.5.3 Work Platform

Size and extent of platform: If two ports are required at 90 degrees the work platform should serve that half of the stack circumference between the ports and extend at least 1.2 metres beyond each port. If four ports are required at 90 degrees, the work platform should serve the entire circumference of the stack. The minimum platform width shall be always 1.2 metres regardless of diameter of stack and number of sampling ports. The detail dimension of platform are shown in Figure 2.6.

2.5.4 Platform Access

Safe and easy access to the work platfrom should be provided via caged ladder, stairway, or other suitable means.

Guardrails, Ladderwells and Stairwells

A safe guardrail should be provided on the platform. Angular rather than round rail members should be used, if possible. No ladderwell, stairwell, or other such openings should be located within 1 metre of any port. Ladderwells should be covered at the platform. Any stairwell leading directly to the platform should be equipped with a safety bar at the opening.

2.5.5 Platform Loading

The work platform should be able to support at least three men (average 80 kg each) and 91 kg of test equipment (stack monitoring kit, etc.). If the stack exists through a building roof, the roof may suffice as the work platform, provided the minimum test site requirements are still met.

2.5.6 Clearance Zone

A three-dimensional, obstruction-free clearance zone should be provided around each port. The zone should extend 0.6 m above, below, to either side of the port. The zone should extend outward from the exterior wall of the stack to a distance of at least 3 metres The clearance zone is illustrated in Figure 2.

Power Supply

Power sources shall be as follows:

a. Platform-one 220 volt, 15 amp, single phase AC circuit with a grounded, two receptacle weatherproof outlet.

b. Stack base-one 220 volt, 15 amp, single phase AC circuit with a grounded, two receptacle weatherproof outlet.

2.5.7 Vehicle Access and Parking

Except for situations in which sampling operations must be conducted from a rooftop or similar structure, stack sampling is sometimes coordinated and controlled from a monitoring van, which is parked near the base of the stack for the duration of the sampling period. Vehicle access and parking space must be provided, since various equipment transport lines will be strung from the monitoring van to the stack platform and will remain in position during the operation.

2.5.8 Additional Requirements

In addition to above aspects the sampling platform, guard rails etc. should be regularly painted and checked for corrosion. There should be no leakages around the sampling port (specially needed for stacks emitting corrosive chemicals).

If anticorrosive lining is done inside the chimney, the same should be extended to the projected portion of the sampling port, monolithically. It has been observed that due to improper lining at the port, the chimney life is reduced considerably. The sampling port should be air tight and no moist air should be allowed to enter the chimney.

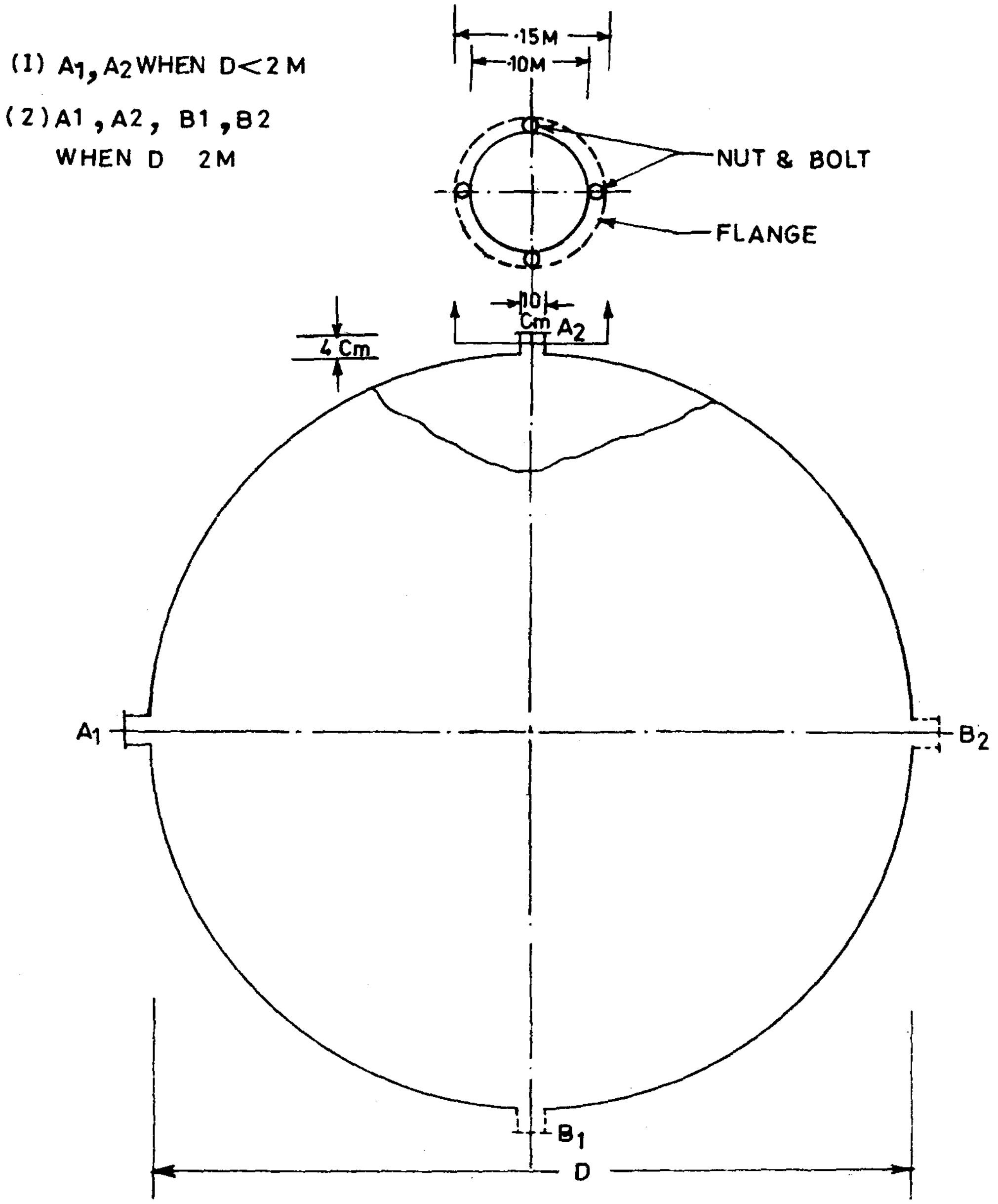
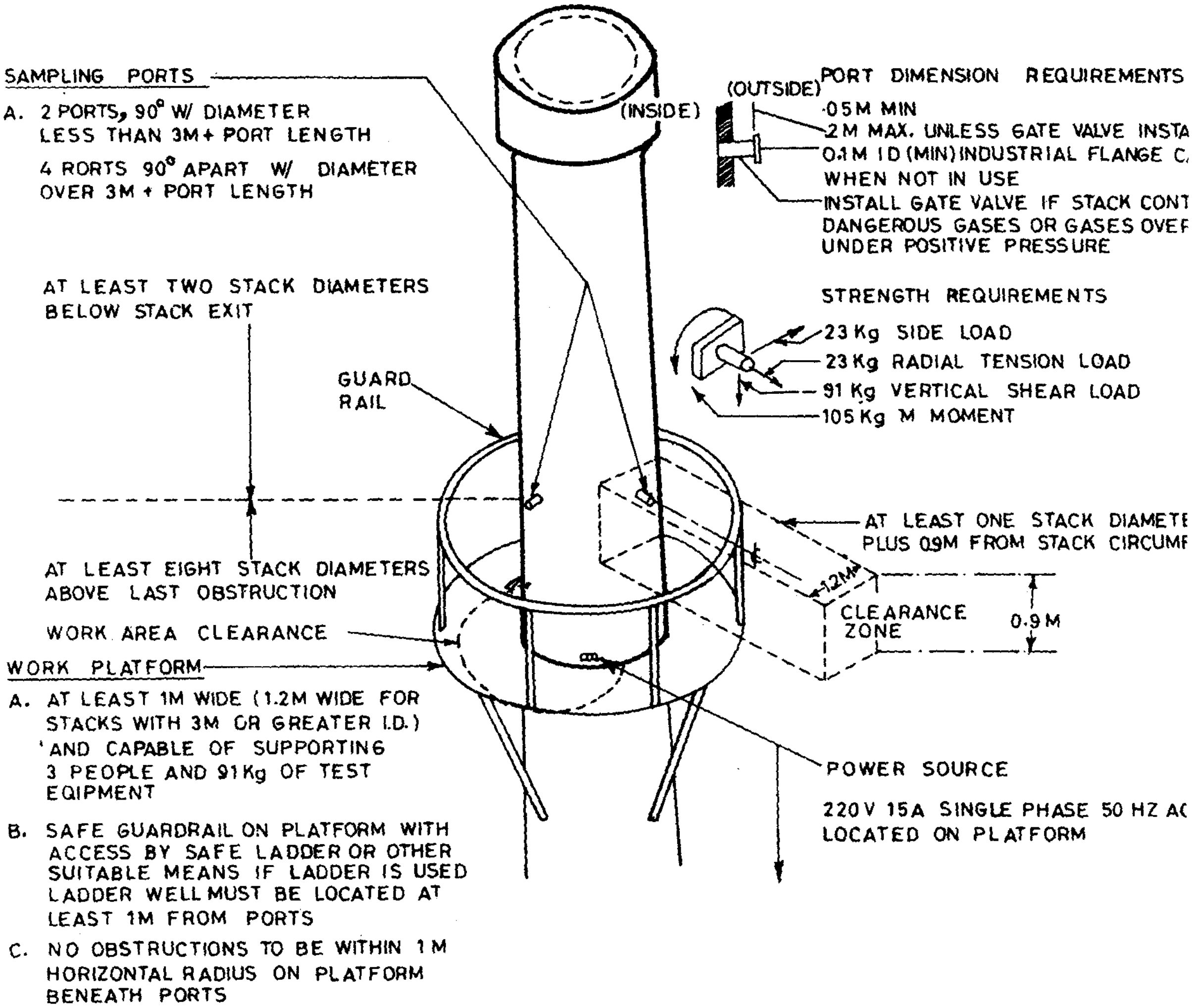


FIGURE 2.5 POSITION OF SAMPLING PORTS IN A CIRCULAR CHIMI

FIGURE 4.1 SO_2 SAMPLING TRAIN



SAMPLING PORTS

A. 2 PORTS, 90° W/ DIAMETER LESS THAN 3M + PORT LENGTH

4 RORTS 90° APART W/ DIAMETER OVER 3M + PORT LENGTH

AT LEAST TWO STACK DIAMETERS BELOW STACK EXIT

AT LEAST EIGHT STACK DIAMETERS ABOVE LAST OBSTRUCTION

WORK AREA CLEARANCE

WORK PLATFORM

A. AT LEAST 1M WIDE (1.2M WIDE FOR STACKS WITH 3M OR GREATER I.D.) AND CAPABLE OF SUPPORTING 3 PEOPLE AND 91 Kg OF TEST EQIPMENT

B. SAFE GUARDRAIL ON PLATFORM WITH ACCESS BY SAFE LADDER OR OTHER SUITABLE MEANS IF LADDER IS USED LADDER WELL MUST BE LOCATED AT LEAST 1M FROM PORTS

C. NO OBSTRUCTIONS TO BE WITHIN 1 M HORIZONTAL RADIUS ON PLATFORM BENEATH PORTS

PORT DIMENSION REQUIREMENTS

·05 M MIN

.2 M MAX. UNLESS GATE VALVE INSTA

0.1 M I D (MIN) INDUSTRIAL FLANGE C, WHEN NOT IN USE

INSTALL GATE VALVE IF STACK CONT DANGEROUS GASES OR GASES OVEF UNDER POSITIVE PRESSURE

STRENGTH REQUIREMENTS

23 Kg SIDE LOAD

23 Kg RADIAL TENSION LOAD

91 Kg VERTICAL SHEAR LOAD

105 Kg M MOMENT

AT LEAST ONE STACK DIAMETE PLUS 0.9M FROM STACK CIRCUMF

POWER SOURCE

220 V 15A SINGLE PHASE 50 HZ AC LOCATED ON PLATFORM

FIGURE 2.6 TYPICAL SAMPLING PROVISION

CHAPTER-3

METHOD FOR MEASUREMENT OF EMISSION FROM STATIONARY SOURCES

3.0.0 This method is for sampling of particulate matter in a moving gas stream in a duct or a stack. The methods for determining the sulphur dioxide and total fluorides are given in Chapters 4 and 5.

3.1.0 The collector recommended for use under specified field conditions is shown and its use to obtain satisfactory results is described. These procedures utilize particulate filtering systems which are located within the stack. If properly used, these systems are satisfactory for determining the mass concentration of particulate matter in the gas stream at stack conditions. The use of collection systems located outside the stack for collecting samples at other than in-stack conditions is an alternative.

3.2.0 Determination of the particulate concentration consists of sampling isokinetically a measured amount of gas from the flue and separating the particles from the gas and hence determining the particulate concentration. To obtain a representative particulate sample, the sampling should be carried out isokinetically, that is, the kinetic energy of the gas stream in the stack should be equal to kinetic energy of the gas stream through the sampling nozzle.

3.2.1 Sampling at otherthan isokinetic velocities induces errors for two reasons. First, sampling at greater or less than isokinetic rates tends to cause respectively a larger or a smaller volume to be withdrawn from the flue than accounted for by the cross-sectional area of the probe, secondly, particles greater than 3.5 micron in size have sufficient intertia so that particle motion may deviate significantly from the gas flow streamline pattern.

In that case, particles are selectively drawn into the probe in a size distribution different from that existing in the duct or flue. It has been observed that, if sampling velocity is greater than the isokinetic rate, the sampling will have a lower mass concentration of particulate material than the main stream because of greater percentage of fine particles. However, if the sampling velocity is less than the isokinetic rate, the particulate sample has a higher mass concentration than actually present, with lower concentration of fine particles. The sampling consists of several distinct steps as already described.

3.3.0 The specific formula for each is given below.

3.3.1 Determination of Molecular Weight

The average molecular weight of the gas mixture is described by the expression:

$$M = \sum_{i=1}^{n} x_i M_i$$

where x_i is the mole fraction and M_i the mole weight of each constituent in the mixture of n number of constituents.

3.3.2 Dry and Wet Molecular Weights

For the majority of sources, Equation 1 is used to calculate the dry molecular weight of the sample. This equation may be modified with additional terms if other gaseous constituents that will influence the molecular weight of the sample are present. Equation 2 is used to calculate the molecular weight of the stack gas on a wet basis.

$$M_d = 0.44\ (\%CO_2) + 0.32\ (\%O_2) + 0.28\ (\%N_2 + \%CO) \qquad 1$$

$$M_s = M_d\ (1 - B_{wo}) + 18\ B_{wo} \qquad 2$$

0.44 — molecular weight of carbon dioxide divided by 100, kg/kg-mole

0.32 -- molecular weight of oxygen divded by 100, kg/kg-mole

0.28 — molecular weight of nitrogen and carbon monoxide divided by 100, kg/kg-mole

B_{wo} — proportion by volume of water vapour in stack gas

18 — molecular weight of water, kg/kg-mole

NOTE -- $\% N_2$ is calculated using the difference method. In the majority of cases the following equation may be used:

$$\% N_2 = 100 - (\% CO_2 \text{ avg} + \% O_2 \text{ avg.} + \% CO \text{ avg.})$$

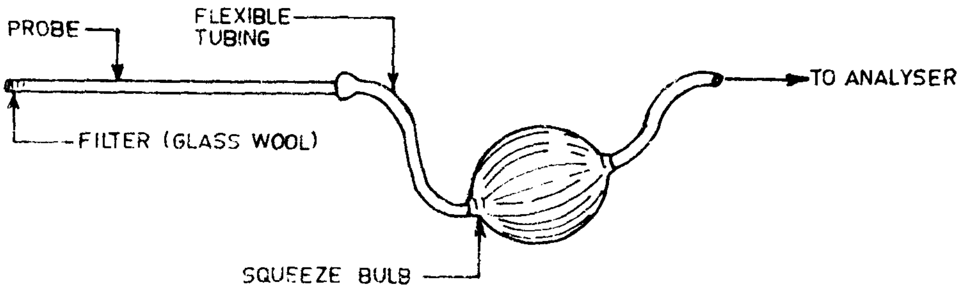


FIGURE 3.1 GRAB SAMPLE TRAIN

where

M_d = Molecular weight of stack gas on dry basis, kg/kg-mole

M_s = Molecular weight of stack gas on wet basis, kg/kg-mole

$\%CO_2$ = Percent carbon dioxide by volume, dry basis

$\%O_2$ = Percent oxygen by volume, dry basis

$\%N_2$ = Percent nitrogen by volume, dry basis

3.4.0 Stack Gas Velocity

$$U_s = K_p \; C_p \; (\Delta P)^{1/2} \; \left(\frac{Ts}{(P_s \, M_s)}\right)^{1/2}$$

where

U_s = Stack gas velocity, m/s

K_p = Constant, 33.5 $\left[m/s \left(\frac{Kg.mm\ Hg}{Kg\text{-}mole\,^{\circ}K\,mmH_2O} \right)^{1/2} \right]$

C_p = S-type pitot tube coefficient

T_s = Absolute stack gas temperature, $^{\circ}K$

ΔP = Stack gas velocity pressure, mm water column

P_s = Absolute stack gas pressure, mm Hg

M_s = Molecular weight of stack gas on wet basis, Kg/kg-mole

3.4.1 Stack Gas Volumetric Flow Rate

The following equation is used to calculate the stack gas volumetric flow rate, Qs (m^3/hr)

$$Qs = 3600\ (U_s) \times As\ (1-B_{wo}) \times \left[\frac{Tref}{Ts}\right] \left[\frac{Ps}{Pref}\right]$$

As = Area of the stack (duct), m^2

B_{wo} = Proportion by volume of water vapour in stack gas

Tref = 298^0 K

Pref = 760 mm

Ts = Absolute stack gas temperature, ^oK

P_s = Absolute stack gas pressure

3.5.0 Determination of Moisture in Gas Stream

3.5.1 Condensor Method - The condensor method, in principle, involves extracting a sample of the stack gases through a filter for removal of the particulate matter, then through a condensor, accumulating the condensate formed in process, and finally through a gas meter. The object of the test is to collect and measure the volume of all the condensate formed at the condensing temperature from a measured amount of gas.

3.5.2 Apparatus - The apparatus necessary for determination of moisture content by the condensate method is given below.

Particulate Sampling Apparatus - consisting of a probe of stainless steel or pyrex glass, sufficiently heated to prevent condensation and equipped with a filter to remove particulate matter.

3.5.3 Condensor equipped with temperature gauge. This may be substituted with two condensor bottles in an ice bucket, each with 30 ml capacity or equivalent. The condensor / condensor bottles are filled with chilled water. The equipment shall be assembled as shown in Figure 4.1 and tested for leaks.

3.5.4 Dry Gas Meter - to measure within 5 percent of the total sample volume.

3.5.5 Gauges - two thermometers (range 0 - 100_{o} C), two calibrated vacuum gauges or U-tube mercury manometers (range 0-500 mm mercury).

3.5.6 Gas Pump - leak-free diaphragm type or equivalent, for sucking gas through sampling apparatus.

3.5.7 Fittings - tubing (rubber, neoprene, etc.), rubber stoppers and flow control (needle-valve and shut-off ball valve).

3.5.8 Procedure - Except in unusual circumstances, the water vapour is uniformly dispersed in the gas stream and therefore sampling for moisture determination need not be isokinetic and is not sensitive to position in the duct. The sampling nozzle may be positioned down-stream to minimize the build-up of pressure drop across the thimble due to particulate catch. Sample the gas at a rate of about 500 ml/sec. Run the test until enough condensate has been collected to enable an accurate measurement. Measure the temperature and pressure of condensor close to the meter, as an insignificant pressure loss in the line between them is expected. The meter pressure may be substituted for condensate pressure. Measure the volume of gas sampled and barometric pressure also in order to calculate the moisture content. Measure the volume of condensate collected in a graduated measuring cylinder.

3.5.9 Calculations

Calculate the volume of water vapour collected using the following equation:

$$V_v = \frac{(V_c \times 22.4)}{1000 \times 18} \times \frac{Tm}{273} \times \frac{760}{P_{bar} - P_m}$$

where

V_v = Equivalent vapour of condensate under sampling conditions, m^3

V_c = Volume of condensate in condensor, ml

T_m = Absolute meter temperature, ^oK

P_m = Suction at meter, mm mercury column

P_{bar} = Barometric pressure, mm mercury column

Calculate the moisture content of the gases using the following equation:

$$M = \frac{V_v}{V_v + V_m} \times 100$$

where

M = Moisture in the flue gases, percent

V_v = Equivalent vapour volume of condensate under sampling condition

V_m = Volume of gas sampled (m^3)

3.6.0 Wet / Dry Bulb Method

The equilibrium temperature attained by water which is vapourizing adiabatically into a gas of constant composition and constant dry bulb or actual temperature, is termed as wet bulb temperature. The amount of depression of the wet bulb temperature below the dry bulb temperature is a function of the degree of saturation of the humidity of the gas. Therefore, the moisture content of the gas can be determined from the wet and dry bulb temperatures.

3.6.1 Calculations - the moisture content may be determined from the test data using a psychrometric chart. The percentage water vapour by volume is found directly. Inputs are the dry bulb temperature and the wet bulb temperature.

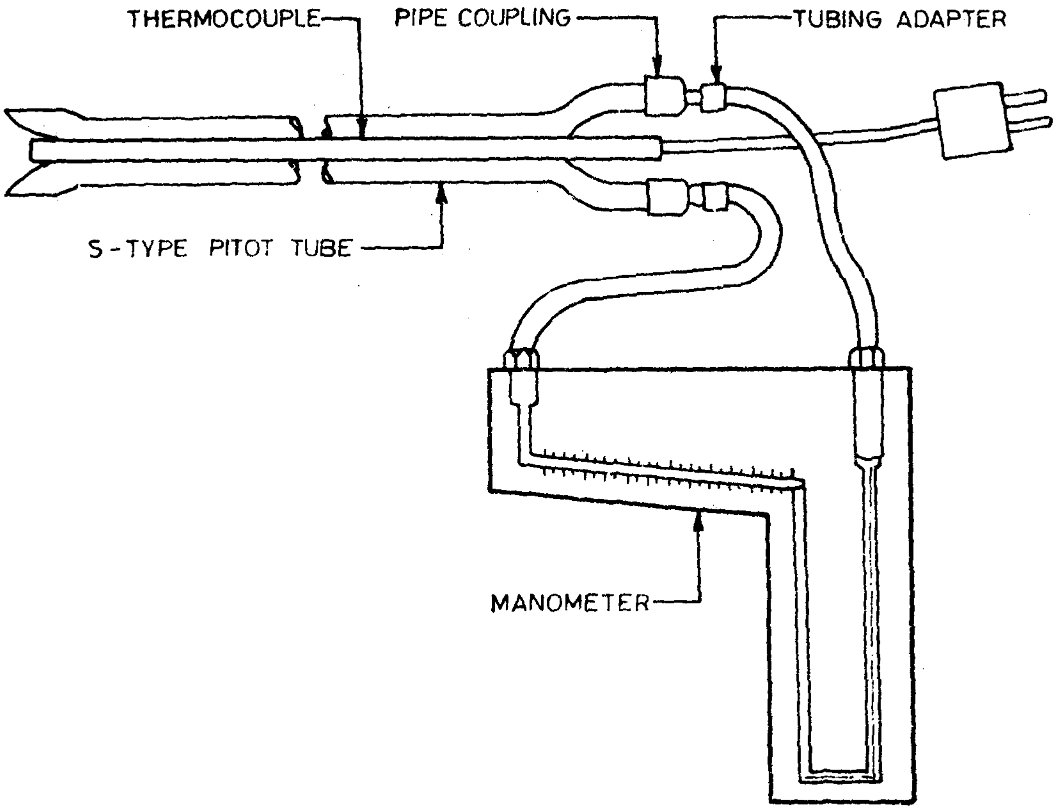


FIGURE 3.2 S-TYPE PITOT TUBE AND MANOMETER ASSEMBLY

3.7.0 **Procedure**

3.7.1 Selection of Location of Sampling - Sample for particulate concentration shall be done at the same traverse points where velocity measurements were carried out.

3.7.2 Calculation of Proper Sampling Rate - The meter for measuring the gas sample measures the gas at conditions of temperature, pressure and moisture content which are different than those in the flue. Therefore, calculate the, sampling rate at the gas meter for each sampling point before starting the test and record on the log the required rate (Table 3.2). Calculate the sampling rate at the gas meter as follows:

$$R_m = U_s \; An \frac{T_m}{T_s} \times \frac{P_{bar} - P_u}{P_{bar} - P_m} \times \frac{V_m}{V_m + V_v}$$

where

R_m = flow rate through meter, m^3/s

U_s = Velocity of flue gas at sampling point, m/s

An = Area of sampling nozzle, m^2

T_m = Absolute meter temperature, ^oK

T_s = Absolute stack gas temperature, ^oK

P_u = Suction in stack, mm mercury column

P_{bar} = Barometric pressure, mm mercury column

P_m = Suction at meter, mm mercury column

V_m = Volume of gas sampled at meter conditions, m^3

V_v = Equivalent vapour volume of condensate at meter conditions, m^3

3.5.3 Select the nozzle size, which will provide a meter sampling rate between 40 to 60 litres/min. Charts relating sampling rate with stack and meter conditions may be prepared for the range of conditions expected.

3.7.4 Duration of Sampling-Deem the run to be of sufficient length if one of the following criteria have been obtained:

a) A minimum of 1 m^3 of dry gas has been withdrawn for sampling.

b) The mass of particulate matter amounts to atleast 20 percent of the mass of the filtering medium in the sampler.

3.7.5 Experience and intelligent judgement should be applied in determining the sampling time. Too short a time may give unreliable results and too long a time may cause the resistance of the sampling train to exceed the pump's limits.

3.8.0 Preparation of the Sampling Train

3.8.1 After proper nozzle and filtering medium have been selected assemble the sample train as shown in Figure 3.3. Mark the sampling probe (including nozzle and filter holder) with the same traverse points used for conducting the velocity traverse.

3.8.2 Place a clean, preweighed thimble in the filter holder and tighten securely.

3.8.3 Start the test after sampling rates have been calculated and train assembled and checked for leakages. When the equipment is ready in all respects, record the initial dry gas meter reading and push the sampling probe carefully into the duct to the point nearest to the back wall. This will allow the probe to cool in hot stack as it comes out, shortening the time required for cooling after the sample is taken. It is advisable to allow the nozzle and filter holder to preheat so that moisture present in the gases does not condense in the filter during initial part of the sampling.

3.8.4 When starting the test, the nozzle should be facing in the up stream direction, start operating the suction source, open the control valve and start the stop watch. Note the time and record it in the log sheet. Adjust the flow rate with the help of the rotameter and control valve until the desired flow rate for isokinetic conditions is obtained. As the test proceeds, dust build-up in the thimble will increase the amount of suction required to maintain the proper meter rate, the valve should be adjusted accordingly. This suction should not exceed 150 mm of mercury for paper thimbles. In case it exceeds this value before the completion of sampling replace the same with a new thimble and restart sampling. During the test if the mercury suction pressure at the meter drops suddenly it indicates that a leak has developed in the equipment or that thimble has cracked or burst. In this event, discard the test and repeat. Record the initial gas meter reading and pressure and temperature in the sampling train as well as condensor temperature at half-minute interval during the test.

3.8.5 When sampling at one point has been completed, move the sampling probe to the next point as quickly as possible. At the completion of test, close the control valve, turn the direction of the probe so that the sampling nozzle is facing down-stream and record the final gas volume and time. Remove the sampler carefully from the flue and plug the nozzle to prevent the loss of sample.

3.9.0 Sample Recovery

After the sampler has cooled, brush down the dust on the inside of the nozzle carefully into the thimble using a small brush remove the thimble and place it in a dust-tight container for transportation to the weighing room. In case the filter holder is kept outside during the sampling, the dust from the sampling probe before the filter holder should be brushed down into the thimble.

3.9.1 Determine the mass of dust collected in the thimble by difference, that is, by weighing the thimble before and after the run. Dry the thimble in an oven for about 2 hours at 120°C prior to sampling. After sampling, cool, dry and again weigh the thimble along with dust maintaining the same conditions as prior to sampling.

3.10.0 Calculations

3.10.1 Calculate the volume of gas sampled using the following equations:

Volume of dry gas through the sampling train (25°C, 760 mm Hg)

$$V_{std} = V_m Y \frac{P_{bar} - P_m}{760} \times \frac{273 + 25}{T_m + 273}$$

where

T_m = Temperature of gas at dry gas meter conditions, °C

V_m = Volume of gas sampled at dry gas meter conditions, m^3

$(P_{bar} - P_m)$ = Actual pressure in sampling train, mm mercury column

P_{bar} = Barometric pressure, mm mercury column

P_m = Static pressure in sampling train, mm mercury column

Y = Calibration factor of dry gas meter.

3.11.0 Dust Concentration - Calculate the dust concentration using the following equations:

Dust Concentration in mg/Nm^3, (25°C, 760 mm Hg, dry basis) $S = \frac{M_n}{V_{std}}$

where

M_n = Mass of the dust in the thimble in mg

V_{std} = Volume of dry gas through the meter (25°C, 760 mm Hg), Nm^3.

3.11.1 Emission Rate - Calculate the dust emission rate as follows:

Dust Emission Rate (kg/hr) $= \frac{S \times Q_s}{10^6}$

where

Q_s = Flue gas flow rate (25°C, 760 Hg mm Hg), Nm^3/hr.

3.12.0 All stack emission test results shall be given in dry basis as in 3.11.0 above, i.e. at zero percent moisture.

Table 3.1
DATA SHEET FOR PARTICULATE MATTER EMISSION FROM POINT SOURCE

Name of the Plant:____________________ **Name of the Project:**____________________

Date	Unit No.	Cross Sectional Area of duct/stack m^2	Stack Temp. ^oC	Velocity m/s	Flow Nm^3/sec	Emission concentration mg/Nm^3.	Mean concentration mg/Nm^3	Emission MT/day	Load MW/ Production (T)	Emission T/MW Production (T)

Table 3.2
DUST CONCENTRATION MEASUREMENTS
LOG SHEET

Job: Time:

Sampling Location: Date: Testing:

Barometric Pressure, P_{bar} (mm, mercury column)

Sampling Point	DRY GAS METER READING					ROTAMETER DETAILS	
	Temperature ^{o}C Tm	Static Pressure mm, Hg Pm	Meter Reading m^3			Sampling Period sec t	Flow Rate m^3/sec Rm
			Initial	Final	Volume sampled Vm		

Check total gas sampled by dry gas meter must be within ± 5 percent of calculated value from rotameter setting multiplied by sampling period.

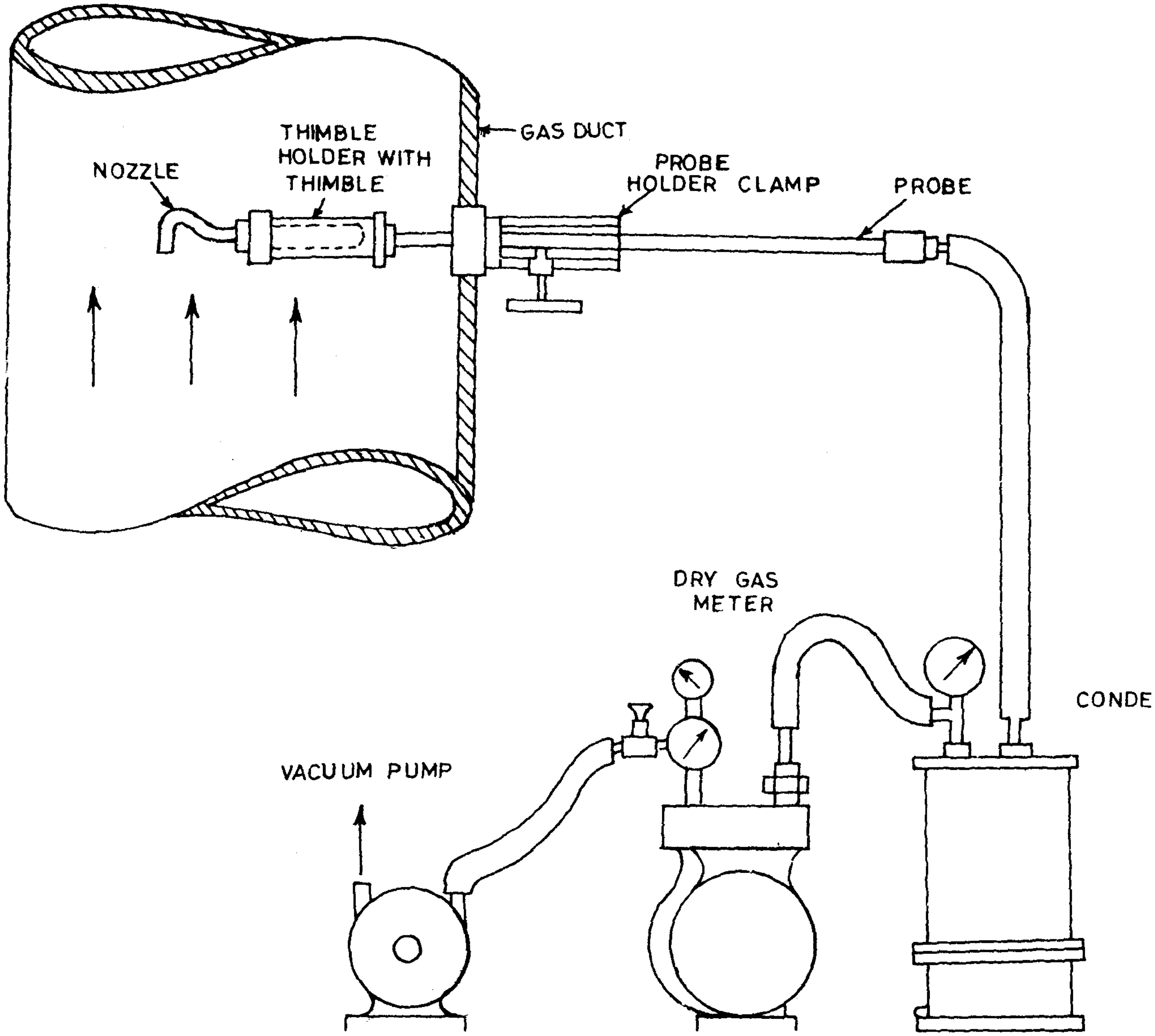


FIGURE 3.3 THIMBLE SAMPLING TRAIN

CHAPTER-4

4.0.0 Determination of Sulphur Dioxide Emission from Stationary Sources (EPA Method)

4.0.1 Principle

A gas sample is extracted from the sampling point in the stack. The sulphuric acid mist (including sulphur trioxide) and the sulphur dioxide are separated. The sulphur dioxide fraction is measured by the barium-thorin titration method.

4.0.2 Applicability

This method is applicable for the determination of sulphur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO_2/m^3. Although no upper limit has been established tests have shown that concentrations as high as 80,000 mg/m^3 of SO_2 can be collected efficiently in two midget impingers, each containing 15 millilitres of 3 percent hydrogen peroxide at a rate of 1.0 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-litre sample is about 93,300 mg/m^3.

Possible interferents are free ammonia, water soluble cations and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not effect the SO_2 analysis.

4.1.0 Apparatus

The sampling train is shown in Figure 4.1.

4.1.1 Probe - Borosilicate glass, or stainless steel, approximately 6 mm inside diameter, with a heating system to prevent water condensation and a filter (either in stack or heated outside stack) to remove particulate matter, including sulphuric acid mist. A plug of glass wool is a satisfactory filter.

4.1.2 Bubbler and Impingers - One midget bubbler, with medium - coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 4.1) to prevent sulphuric acid mist carry over, and three 30 ml midget impingers. The bubbler and midget impingers must be connected in series with leak free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

4.1.3 Glass Wool - Borosilicate or quartz.

4.1.4 Stop Cock Grease - Acetone-insoluble heat stable silicone grease may be used, if necessary.

4.1.5 Temperature Gauge - Dial thermometer or equivalent, to measure temperature of gas leaving impinger train to within $1^{\circ}C$.

4.1.6 Drying Tube - Tube packed with 6 to 16 mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If the silica gel has been used previously, dry at $175^{\circ}C$ for 2 hours. New Silica gel may be used as received.

4.1.7 Valve - Needle Valve, to regulate sample gas flow rate.

4.1.8 Pump - Leak free diaphragm pump, or equivalent to pull gas through the train.

4.1.9 Rate Meter - Rotameter, or equivalent capable of measuring flow rate to within 2 percent of the selected flow rate of about 1000 cc/min (1 lpm).

4.1.10 Volume Meter - Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling and equipped with a manometer for measuring static pressure and a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 0.5°C.

4.1.11 Barometer - Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby meteorological station.

4.2.0 Reagents - Only AR grade reagents for sampling and analysis should be used. Other specifications for sampling materials as given below.

4.2.1 Water - Deionized water

4.2.2 Isopropanol, 80 percent - Mix 80 ml of isopropanol with 20 ml of deionized, distilled water. Check each lot of isopropanol for peroxide impurities as follows:

Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance at 352 nanometers on a spectrophotometer. If absorbance exceeds 0.1, reject alcohol for use.

4.2.3 Hydrogen Peroxide, 3 percent - Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deinoized, distilled water (30 ml is needed per sample). Prepare fresh daily.

4.2.4 Potassium Iodide (KI) Solution; 10 percent - Dissolve 10.0 gram KI in deionized distilled water and dilute to 100 ml, prepare when needed.

4.3.0 Specifications for analytical materials as given below.

4.3.1 Water - Deionized water.

4.3.2 Isopropanol; 100 percent.

4.3.3 Thorin Indicator - 1-(O-arsonophenylazo)-2-naphthol-3,6-disulphonic acid, disodium salt, or equivalent. Dissolve 0.20 gm in 100 ml of deionized, distilled water.

4.3.4 Barium Perchlorate Solution 0.0100 N - Dissolve 1.95 gm of barium perchlorate trihydrate $Ba(Cl0_4)_2 . 3\ H_2O$ in 200 ml distilled water and dilute to 1 litre with isopropanol. Alternatively, 1.22 gm of $BaCl_2 . 2H_2O$ may be used instead of the perchlorate.

4.3.5 Sulphuric Acid Standard; 0.0100 N - Standardised to 0.0002 N against 0.0100 N NaOH which has been previously standardised against potassium acid phthalate.

4.4.0 Procedure

4.4.1 Sampling

Preparation of Collection Train - Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 4.1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers and bubbler.

4.4.2 Leak Check Procedure

A leak check prior to the sampling run is optional, however, a leak check after the sampling run is mandatory.

The leak check procedure is as follows:
Temporarily attach a suitable (e.g. 0 to 3 lpm) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

Note: Carefully release the probe inlet plug before turning off the pump.

4.4.3 Sample Collection

Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point. Adjust the sample flow rate to a constant rate of approximately 1.0 litre/minute as indicated by the rotameter. Maintain this constant rate (within ±10 percent) during the entire sampling run. Take readings (dry gas meter, and rotameter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20°C or less. At the end of each run, turn off the pump, remove probe from the stack and record the final readings.

4.4.4 Sample Recovery

Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with deionized distilled water, and add the washings to the same storage container. Mark the fluid level, seal and identify the sample container.

4.4.5 Sample Analysis

Transfer the contents of the storage container to a 100 ml volume with deionized, distilled water. Pipette a 20 ml aliquot of this solution into a 250 ml-Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml whichever is larger.

4.4.6 Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data.

4.4.7 Nomenclature

C_{SO_2} = Concentration of sulphur dioxide, dry basis converted to standard conditions, mg/Nm^3

N = Normality of barium perchlorate titrant milliequivalents/ml

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg

P_{std} = Standard absolute pressure, 760 mm Hg

T_m = Average dry gas meter temperature, ^oK

T_{std} = Standard temperature, 298^oK

V_a = Volume of sample aliquot-titrated, ml

V_m = Dry gas volume as measured by the dry gas meter, m^3

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, Nm^3

V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titration)

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Equivalent weight of SO_2

4.4.8 Dry sample gas volume, corrected to standard conditions

$$V_{m(std)} = V_m \, Y \, \frac{T_{std}}{T_m} \times \frac{P_{bar}}{P_{std}}$$

$$= \frac{K_1 Y V_m P_{bar}}{T_m}$$

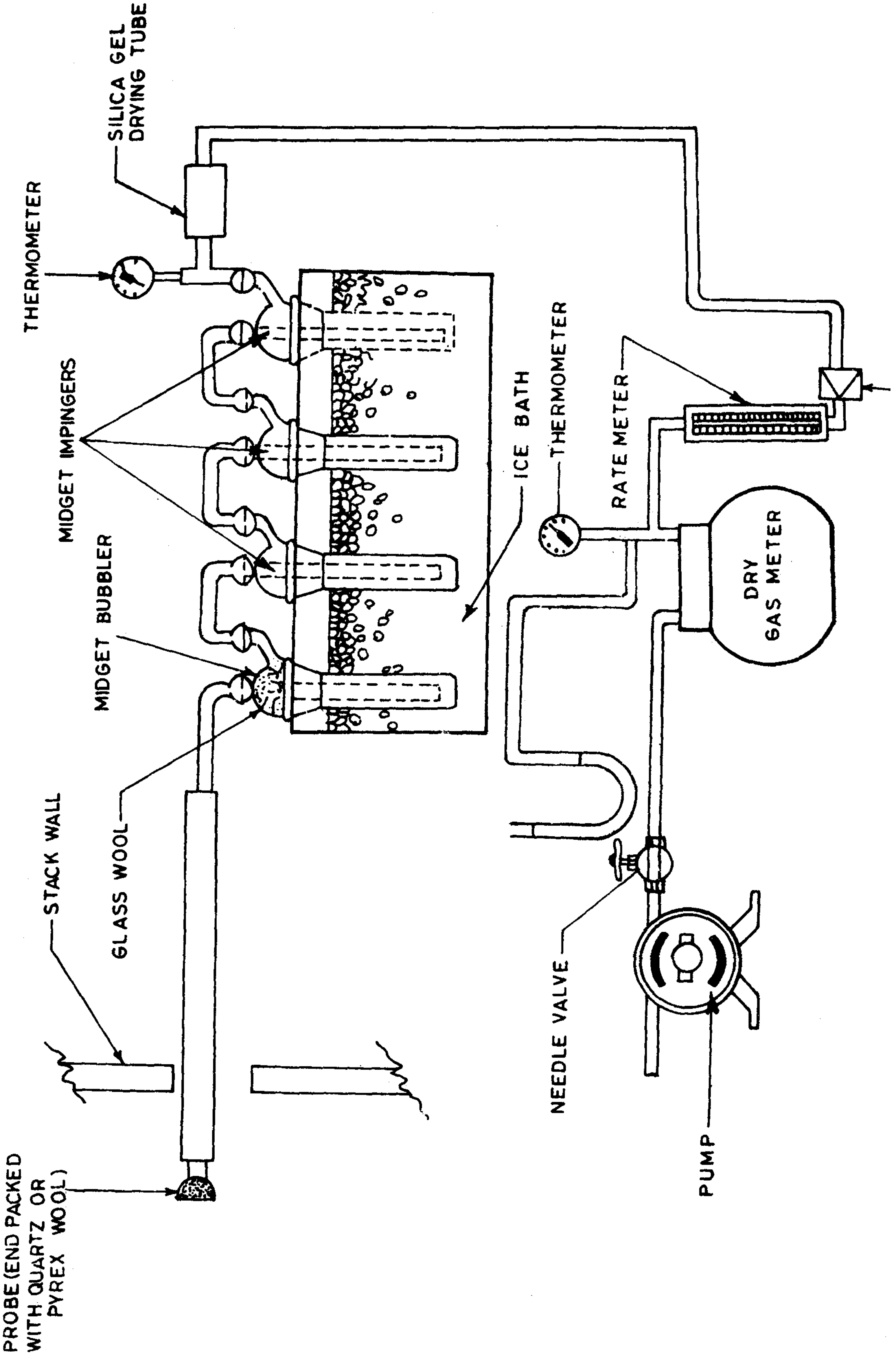
K_1 = 0.3858° K/mm Hg

4.4.9 Sulphur dioxide concentration

$$C_{SO_2} = \frac{K_2 \, (V_t - V_{tb}) \, N \, \frac{(V_{soln})}{V_a}}{V_{m(std)}}$$

where

K_2 = 32.03 mg/meq.


PROBE (END PACKED WITH QUARTZ OR PYREX WOOL)
STACK WALL
GLASS WOOL
MIDGET BUBBLER
MIDGET IMPINGERS
THERMOMETER
SILICA GEL DRYING TUBE
ICE BATH
THERMOMETER
RATE METER
DRY GAS METER
NEEDLE VALVE
PUMP

CHAPTER-5

5.0.0 Determination of Total Fluoride Emissions from Stationary Sources - Specific Ion Electrode Method (EPA Method)

5.0.1 Applicability

This method applies to the determination of fluoride (F) emissions from stationary sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

5.0.2 Principle

Gaseous and particulate fluorides are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the specific ion electrode method.

5.0.3 Range and Sensitivity

The range of this method is 0.02 to 2.000 μg F/ml; however, measurements of less than 0.1 μg F/ml require extra care.

5.0.4 Interferences

Grease on exposed surfaces may cause low F results because of absorption.

5.1.0 Apparatus

5.1.1 Sampling Train and Sample Recovery - Same as method for SO_2 determination from stationary sources.

5.2.0 Analysis

5.2.1 Distillation apparatus, Bunsen burner, electric muffle furnace, crucibles, beakers, volumetric flasks, Erlenmeyer flask or plastic bottles, constant temperature bath, and balance.

5.2.2 Fluoride Ion Activity Sensing Electrode.

5.2.3 Reference Electrode - Single junction, sleeve type.

5.2.4 Electrometer - A pH meter with millivolt-scale capable of 0.1 mv resolution or a specific ion meter made specially for specific ion use.

5.2.5 Magnetic Stirrer and Fluorocarbon-Coated Stirring Bars.

5.3.0 Reagents

Analysis - Use the following AR grade chemicals (or equivalent) unless otherwise specified.

5.3.1 Calcium Oxide (CaO) - Certified grade containing 0.005 percent F or less.

5.3.2 Phenolphthalein Indicator - Dissolve 0.1 gm of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml deionized distilled water.

5.3.3 Sodium Hydroxide (NaOH) - Pellets.

5.3.4 Sulphuric Acid (H_2SO_4) - Concentrated.

5.3.5 Filters - Whatman No. 541 or equivalent.

5.3.6 Sodium Hydroxide 5 M - dissolve 20 gm of NaOH in 100 ml of deionized distilled water.

5.3.7 Sulphuric Acid, 2.5 percent (V/V) - Mix 1 part of concentrated H_2SO_4 with 3 parts of deionized distilled water.

5.3.8 Total Ionic Strength Adjustment Buffer (TISAB) - Place approximately 500 ml of deionized distilled water in a 1 litre beaker. Add 57 ml of glacial acid, 58 gm of sodium chloride, and 4 gm of cyclohexylene - dinitro - tetraacetic acid. Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-litre volumetric flask, and dilute to volume with deionized distilled water. Commercially prepared TISAB may be substituted for the above.

5.3.9 Fluoride Standard solution, 0.1 M - Oven dry some sodium fluoride (NaF) for a minimum of 2 hours ar 110°C, and store in a dessicator. Then add 4.2 gm of NaF to a 1-litre volumetric flask and add enough deionized distilled water to dissolve. Dilute to volume with deionized distilled water.

5.4.0 Procedure

Sampling, sample recovery, and sample preparation and distillation.

Container No. 1 - Probe, filter and impinger catches, use a graduated cyclinder, measure to the nearest ml, and record the volume of the water in the first of these impingers, include any condensate in the probe in this determination. Transfer the impinger water from the graduated cylinder into this polyethylene container. Add the filter to this container, taking care that dust on the outside of the probe of other exterior surface does not get into the sample. Clean all sample exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors and filter holder) with deionized distilled water. Use less than 500 ml for the entire wash. Add the washings to the sampler container. Perform the deionized distilled water rinses as follows:

Carefully remove the probe nozzle and rinse the inside surface with deionized water from a wash bottle. Brush with a nylon bristle brush and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with deionized distilled water in a similar way.

Rinse the probe liner with deionized distilled water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surface will be wetted with water. Let the water drain from the lower end into the sample container. A funnel (glass or polyethlene) may be used to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt deionized distilled water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With a stainless steel or other metal probe, run the brush through, in the above prescribed manner at least six times, since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with deionized distilled water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Rinse the inside surface of each of the first three impingers (and connecting glassware) three separate times. Use a small portion of deionized distilled water for each rinse, and brush each sample-exposed surface with a nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush.

After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with deionized distilled water the inside of the filter holder (front-half only, if filter is positioned between the third and fourth impingers). Brush and rinse each surface three times or more if needed. Make a final rinse of the brush and filter holder.

After all water washings and particulate matter have been collected in the sampler container, tighten the lid so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

Container No. 2 (Sample Blank) - Prepare a blank by placing an unused filter in a polyethylene container and adding a volume of water equal to the total volume in Container No. 1. Process the blank in the same manner as for Container No. 1.

5.5.0 Analysis

5.5.1 Containers No. 1 and No.2 - Distill suitable aliquots from Container No. 1 and No. 2 (apparatus shown in Figure 5.2). Dilute the distillate in the volumetric flask to exactly 250 ml with deionized, distilled water and mix thoroughly. Pipette 25 ml aliquot from each of the distillate and separate beakers. Add an equal volume of TISAB and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than ±2°C from the temperature at which the calibration standards were measured, condition samples and standards in a constant temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. if the sitrrer generates enough heat to change solution temperature, place a piece of temperature insulating material such as cork, between the stirrer and the beaker. Hold dilute samples (below 10^{-4}M fluoride ion content) in polyethylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with deionized distilled water.

5.6.0 Calibration

Maintain a laboratory log of all calibrations.

5.6.1 Sampling Train - Same as method for determination of SO_2, shown in Figure 5.1.

5.6.2 Fluoride Electrode - Prepare fluoride standardizing solutions by serial dilution of the 0.1 M flouride standard solution. Pipette 10 ml of 0.1 M fluoride standard solution into a 100 ml volumetric flask and make up to the mark with deionized distilled water for a 10^{-2} M standard solution. Use 10 ml of 10^{-2} M solution to make a 10^{-3} M solution in the same manner. Repeat the dilution procedure and make 10^{-4} M and 10^{-5} M solutions.

Pipette 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis e.g. when 50 ml of 10^{-2} M standard is diluted with 50 ml of TISAB the concentration is still designated "10^{-2} M".

Between measurements soak the fluoride sensing electrode in deionized distilled water for 30 seconds, and then remove and blot dry. Analyze the standards, going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} fluoride molarity on the log axis plotted versus electrode potential (in mV) on the linear scale. Some electrodes may be slightly nonlinear between 10^{-5} M and 10^{-4} M. If this occurs, use additional standards between these two concentrations.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10^{-2} M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

Note: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride.

5.7.0 Calculations

Carry out calculations, retaining atleast one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

5.7.1 Nomenclature

M = F concentration from calibration curve, molarity.

V_t = Total volume of F in sample, after final dilution, ml.

A_t = Aliquot of total sample added to still, ml

V_d = Volume of distillate as diluted, ml

F_t = Total F in sample, mg

5.7.2 Fluoride in Sample - Calculate the amount of F in the sampling using the following equation:

$$F_t = \frac{V_t}{A_t} (V_d) (M)$$

5.7.3 Fluoride Concentration in Stack Gas - Determine the fluoride concentration in the stack gas, C_s, using the following equation:

$$C_s = \frac{F_t}{V_{m(std)}}$$

where

$V_{m(std)}$ = Volume of gas sample as measured by dry gas meter, corrected to standard conditions.

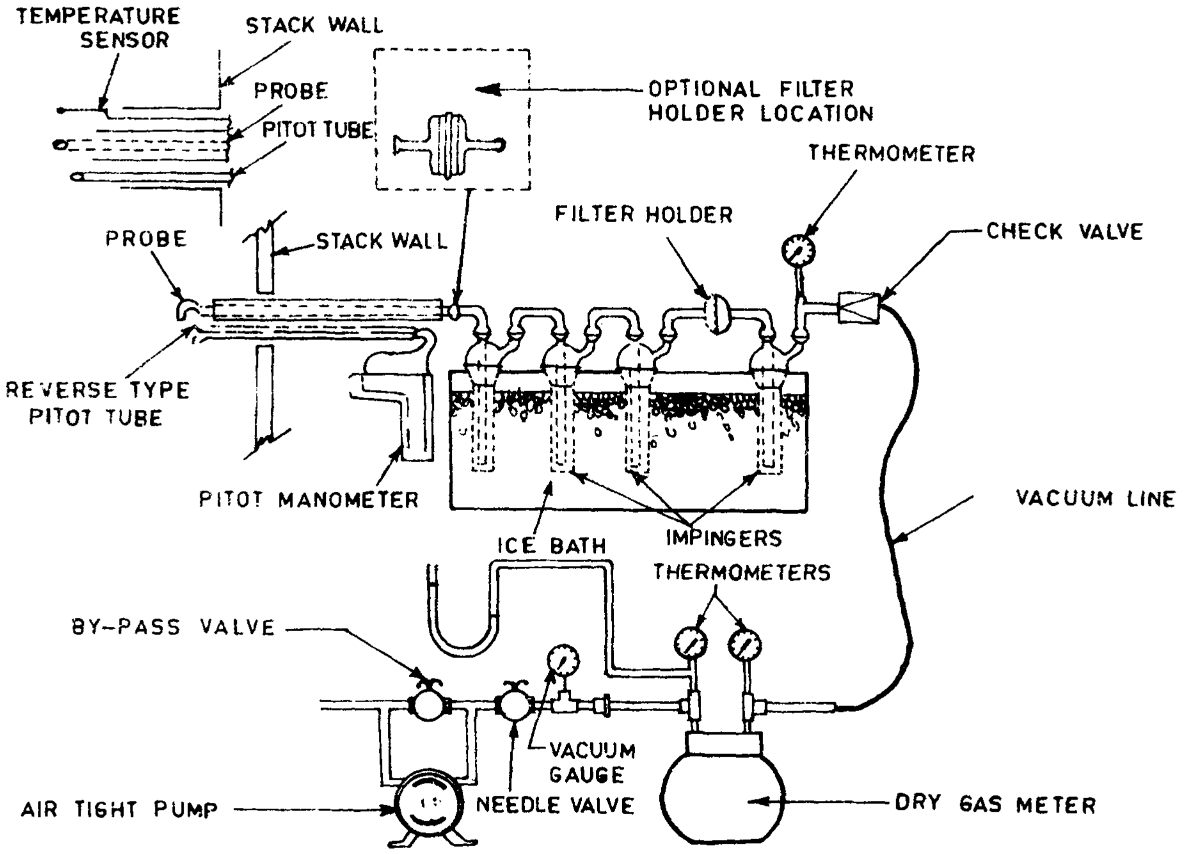


FIGURE 5.1 FLUORIDE SAMPLING TRAIN

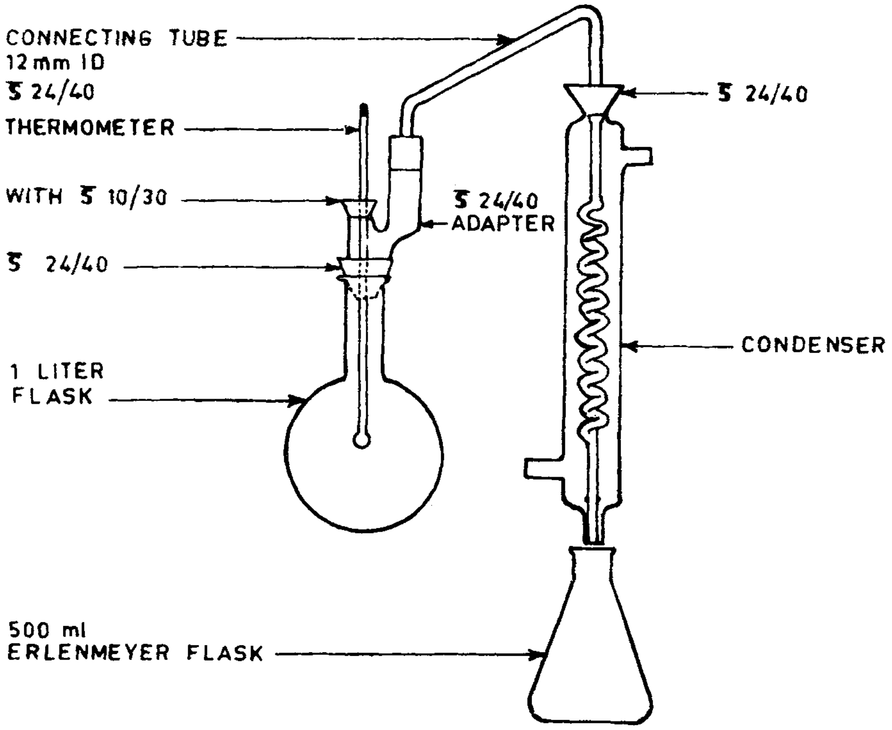


FIGURE 5.2 FLUORIDE DISTILLATION APPARATUS

CHAPTER-6

6.0.0 Ambient Air Quality Monitoring

This section deals with the methods of ambient air quality monitoring. The industries that are required to do this are given in Chapter 1.

6.0.1 Certification

A high volume sampler may be used for measuring suspended particulate matter with a provision for measuring pollutant gases. A low volume sampler may be used for measuring ambient quantities of gaseous pollutants. Alternatively, properly calibrated automatic continuous monitors may be used for this purpose.

6.0.2 The high and low volume samplers as well as the automatic continuous monitors should be approved by the Central Pollution Control Board.

6.0.3 The group or laboratory performing the test should have to be approved by the Central Board in those cases where the results of the tests are being submitted to the Central Board or the State Boards. Where a dispute occurs, this will be resolved by the tests being conducted by the Central Board itself or its approved laboratory.

6.1.0 Specifications of High Volume Air Sampler

6.1.1 General

High volume sampler complete in all respects including blower, filter holder free from leakages, cabinet, roof shelter, automatic voltage stabilizer, flow measurement device and arrangement of gaseous sampling with flow controller. Dimensions of high volume sampler are given in Figure 6.1.

6.1.2 Blower Flow Rate

1.4 to 1.8 m^3/min free flow (without resistance)

6.1.3 Voltage Stabilizer

An automatic voltage stabilizer to keep the voltage between 210 and 230 V at 50 to 60 Hz shall be provided.

6.1.4 Filter Holder

A stainless steel (SS 304) filter holder assembly with rubber gasket to hold 25 cm x 20 cm (10 in x 8 in) filter paper.

Net size of filter paper for suction after putting the filter holder frame shall not be less than 23 cm x 18 cm.

6.1.5 Gaseous Sampling

The gas inlet should be kept on the pipe after the cast aluminium hopper but before the blower. There can be three inlets for different gases or one inlet through a manifold. A calibrated rotameter (0 to 3 lpm) shall be provided for checking the flow rate.

6.1.6 Particulate Sampling

The inlet openings in the housing to the filter shall be such that particles collecting on the filter surface are less than 100 microns. This will be done by keeping the angle of the gable roof at 45^o to the horizontal.

6.1.7 Main Housing

The main housing on castors shall be rectangular (29 cm and 36 cm) and made of unpainted sturdy aluminium.

6.1.8 Automatic Timer and Time Totalizer

The samples should have a timer for 4 to 24 hour of setting with intermediate on-off. It should have in addition, a time totalizer to indicate hours and minutes.

6.1.9 Calibration

The blower should be calibrated against a standard orifice/ meter or a U-tube manometer. The graph in case of the U-tube manometer should be fixed on the sampler. The calibration certificate from the manufacturer of the rotameter should accompany the sampler.

6.2.0 Method of Sampling

The sampling and analysis method for suspended particulate matter shall be as per Indian Standard Method for Measurement of Air Pollution; IS: 5182 (Part IV) 1973. The filter paper should be type EPM-2000 Whatman, or equivalent.

6.2.2 The measurement of sulphur dioxide shall be as per Indian Standard Method for Measurement of Air Pollution; IS: 5182 (Part II) 1969.

6.2.3 Nitrogen dioxides shall be analyzed using the Jacob and Hochheiser, modified method, given in Chapter 7.

6.4.2 The measurement of ambient total fluorides shall be as per method given in APHA, given in Chapter 8.

6.3.0 The results shall be reported in the format of Table 6.1.

Table 6.1

AIR QUALITY DATA AT

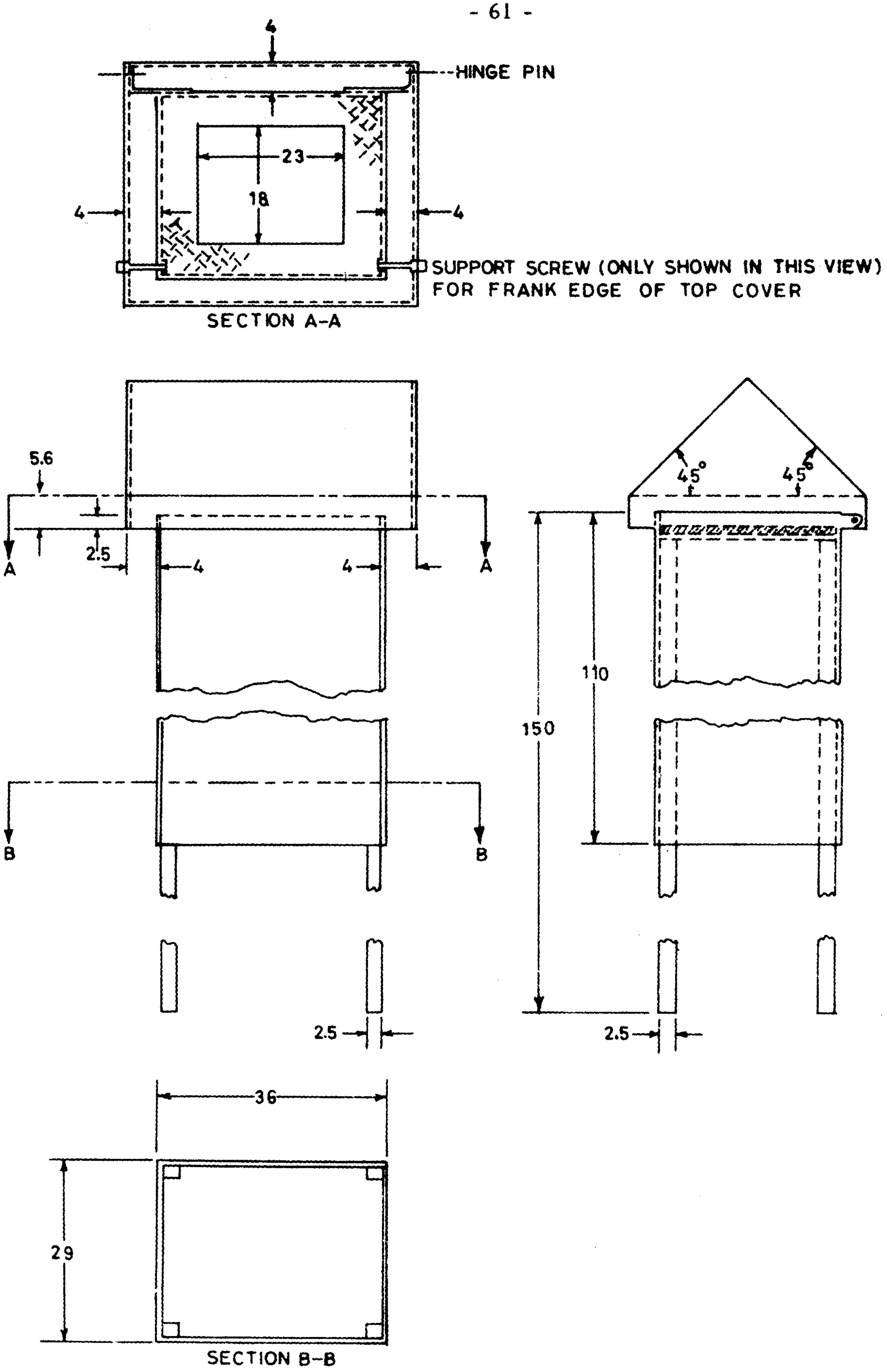
____

SULPHUR DIOXIDE, OXIDES OF NITROGEN AND SUSPENDED PARTICULATE MATTER FOR THE MONTH OF ____________

(IN μG/CU M)

CLOCK HRS DAYS DATES	10 - 14 SO2 NO2	14 - 18 SO2 NO2	18 - 22 SO2 NO2	22 - 02 SO2 NO2	02 - 06 SO2 NO2	06 - 10 SO2 NO2	4-HRLY MAX SO2 NO2	24-HRLY AVERAGE SO2 NO2	SPM
NUMBER OF OBSERVATIONS: ARITHMETRIC MEAN: GEOMETRIC MEAN: STD GEOM DEVIATION MAX CONCENTRATIONS NO. OF OBS 30/40 @									

• (PRECEDED BY BLANK) INDICATES MISSING DATA
S TOTAL NUMBER OF 4-HRLY OBSERVATIONS IN THE MONTH
@ 30 μG/CU M SO2 / 40 μG/CU M NOX
¥ TOTAL NO. OF SO2VALUES > 30 μG/CU M IN MONTH
¥¥ TOTAL NO. OF NOX VALUES > 40 μG/CU M IN MONTH
NO2-JACOBS HOCHHEISER, SODIUM ARSENITE MODIFIED METHOD.- USING TWO IMPINGERS IN SERIES



SUPPORT SCREW (ONLY SHOWN IN THIS VIEW) FOR FRANK EDGE OF TOP COVER

FIGURE 6.1 DETAIL DRAWING OF HIGH VOLUME SAMPLER SHELTER. DIMENSIONS ARE IN CENTIMETERS

CHAPTER-7

7.0.0 Determination of Nitrogen Dioxide in Ambient Air

(Jacob and Hochheiser, modified method)

7.1.0 Principle and Applicability

Nitrogen dioxide is colledted by bubbling air through a sodium hydroxide-sodium arsenite solution to form a stable solution of sodium nitrite. The nitrite ion produced during sampling is reacted with phosphoric acid, sulphanilamide, and N-1 (naphthyl) ethylenediamine dihydrochloride to form an azo dye and then determined colourimetrically.

The method is applicable to collection of 4 to 24 hour samples in the field and subsequent analysis in the laboratory.

7.2.0 Range and Sensitivity

The range of the analysis is 0.04 to 2.0 µg NO_2/ml. Beer's law is obeyed through this range (0 to 1.0 absorbance units). With 50 ml absorbing reagent and a sampling rate of 200 cm^3/min for 24 hours, the range of the method is 20 to 250 µg/m (0.01 to 0.04 ppm) nitrogen dioxide.

A concentration of 0.04 µg NO_2/ml will produce an absorbance of approximately 0.02 with 1 cm cells.

7.3.0 Interference

Nitric oxide is a positive interferent. The presence of NO can increase the NO_2 response by 5 to 15% of the NO_2 sampled.

The interference of sulphur dioxide is eliminated by converting it to sulphate ion with hydrogen peroxide before analysis.

7.4.0 Precision Accuracy and Stability

The relative standard deviations for sampling NO_2 concentrations of 78, 105 and 328 $\mu g/m^3$ are 3, 4 and 2%, respectively. Collected samples are stable for at least 6 weeks.

7.5.0 Apparatus

7.5.1 Volumetric Flask - 50, 100, 200, 250,' 500, 1000 ml.

7.5.2 Graduated Cylinder - 1,000 ml.

7.5.3 Pipettes - 1,2,5,10,15 ml volumetric, 2 ml graduated in 1/10 ml intervals.

7.5.4 Test Tubes - Approximately 20 x 150 mm.

7.5.5 Spectrophotometer - Capable of measuring absorbance at 540 mm.

7.6.0 Reagents

7.6.1 Sodium Hydroxide - AR reagent grade.

7.6.2 Sodium Arsenite - AR reagent grade.

7.6.3 Absorbing Reagent - Dissolve 4.0 gm sodium hydroxide in distilled water, add 1.0 gm of sodium arsenite and dilute to 1,000 ml with distilled water.

7.6.4 Sulphanilamide -Melting point of 165 to 167°C.

7.6.5 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Best grade available.

7.6.6 Hydrogen Peroxide - AR reagent grade 30%.

7.6.7 Sodium Nitrite - Assay of 97% $NaNO_2$ or greater.

7.6.8 Phosphoric Acid - AR reagent grade, 85% minimum.

7.6.9 Sulphanilamide Soln - Dissolve 20 gm sulphanilamide in 700 ml distilled water. Add with mixing, 50 ml concentrated phosphoric acid and dilute to 1,000 ml. This solution is stable for one month, if refrigerated.

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

7.6.11 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 protected from light and refrigerated.

7.6.12 Standard Nitrite Solution - Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1,000 ml so that a solution containing 1,000 μg NO_2^-/ml is obtained. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100$$

where

G = Amount of $NaNO_2$, gm

1.500 = Gravimetric factor in converting NO_2 into $NaNO_2$

A = Assay, percent.

7.7.0 Analysis

Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorption tube. Pipette in 1 ml hydrogen peroxide solution, 10 ml sulphanilamide solution and 1.4 ml NEDA solution with thorough mixing after the addition of each reagent. Prepare a blank in the same manner using 10 ml of unexposed absorbing reagent. After a 10 minute colour-development interval, measure the absorbance at 540 nm against the blank. Read $\mu g\ NO_2^-/ml$ from the calibration curve. Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot (less than 10 ml) of the collected sample with unexposed absorbing reagent.

7.8.0 Calculation

Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

where

V = Volume of air sampled, m^3

F_1 = Measured flow rate at start of sampling, cc/min

F_2 = Measured flow rate at end of sampling, cc/min

T = time of sampling, minutes

10^{-6} = Conversion of cm^3 to m^3.

Calculate the concentration of nitrogen dioxide as $\mu g\ NO_2/m^3$ using:

$$\mu g\ NO_2/m^3 = \frac{(\mu g\ NO_2^-/ml) \times 50}{V \times 0.82}$$

where

50 = Volume of absorbing reagent used in sampling, ml

V = volume of air sampled, m^3

0.82 = Factor for collection efficiency

If desired, concentration of nitrogen dioxide may be calculated as ppm $NO_2 = (\mu g\ NO_2/m^3) \times 5.32 \times 10^{-4}$.

CHAPTER-8

8.0.0 Determination of Total Fluorides in Ambient Air (APHA Method)

8.1.0 Principle

Atmospheric samples are taken using midget impingers containing 10 ml of 0.1 M NaOH.

Samples are diluted 1:1 with Total Ionic Strength Activity Buffer (TISAB). The diluted samples are analyzed using the fluoride ion selective electrode.

8.2.0 Range and Sensitivity

The range and sensitivity have not been established. The recommended range of the method is 0.009 to 95 mg/m^3 air.

8.3.0 Interference

Hydroxide ion is the only significant electrode interference; however, addition of the TISAB eliminates this problem. Very large amounts of complexing metals such as aluminium may result in low readings even in the presence of TISAB.

8.4.0 Precision and Accuracy

The accuracy and precision of this method have not been determined. No collaborative tests have been performed on this methods.

8.5.0 Advantages and Disadvantages of the Method

Advantages over previous methods include simplicity, accuracy, speed, specificity and elimination of distillation, diffusion and ashing of the samples.

No significant disadvantages are known at present.

8.6.0 Apparatus

8.6.1 Sampling Equipment

The sampling unit for the impinger collection method consists of the following components.

8.6.2 A Prefilter Unit - Consists of the filter media and cassette filter holder.

8.6.3 A Midget Impinger - Containing the absorbing solution or reagent.

8.6.4 A pump suitable for delivering desired flow rates.

The sampling pump is protected from splashover or water condensation by an absorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

8.6.5 A rotameter to measure the air flow.

8.6.6 An Orion model 94-09 fluoride selective ion electrode, or equivalent.

8.6.7 Reference Electrode - Orion 90-01 single junction, or equivalent calomel or silver / silver chloride electrode.

8.6.8 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 mV.

8.6.9 Polyethylene beakers 50 ml capacity.

8.6.10 Laboratory Glassware

8.6.11 Magnetic stirrer and stirring bars for 50 ml beakers.

8.7.0 Reagents

8.7.1 Purity - All chemicals must be ACS reagent grade, or equivalent. Polyethylene beakers and bottles should be used for holding and storing all fluoride containing solutions.

8.7.2 Double Distilled Water

8.7.3 Glacial Acetic Acid

8.7.4 Absorbing solution, 0.1 M Sodium Hydroxide Solution - Dissolve 4 gm sodium hydroxide pellets in 1 litre of distilled water.

8.7.5 Sodium Hydroxide, 5 M Solution - Dissolve 20 gm sodium hydroxide pellets in sufficient distilled water to give 100 ml of solution.

8.7.6 Sodium Chloride

8.7.7 Sodium Citrate

8.7.8 Total Ionic Strength Activity Buffer (TISAB) - Place 500 ml of double distilled water in a 1 litre beaker. Add 57 ml of glacial acetic acid, 58 gm of sodium chloride and 0.30 gm of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling) and slowly add 5 M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour to a 1 litre volumetric flask and add double distilled water to the mark.

8.7.9 Sodium Fluoride - for preparation of standards.

8.7.10 Standard Fluoride Solution - Dissolve 4.2 gm of sodium fluoride in double distilled water and dilute to 1 litre. This solution contains = 10^{-1} M[F] (1900 μg F^-/ml). Store in plastic bottle. Reagent is stable for 2 months. Other dilutions should be prepared weekly.

Prepare 10^{-2} M[F] by diluting 10 ml of 10^{-1} M[F] to 100 ml with double distilled water (190 μg F^-/ml).

Prepare 10^{-3} M[F] by diluting 10 ml of 10^{-2} M[F] to 100 ml with double distilled water (19 μg F^-/ml).

Prepare 10^{-4} M[F] by diluting 10 ml of 10^{-3} M[F] to 100 ml with double distilled water (1.9 μg F^-/ml).

Prepare 10^{-5} M[F] by diluting 10 ml of 10^{-4} M[F] to 100 ml with double distilled water (0.19 μg F^-/ml).

8.8.0 Procedure

8.8.1 Cleaning of Equipment

All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with double distilled water.

8.8.2 Collection and Shipping of Samples

8.8.3 Pour 10 ml of the absorbing solution (section 8.7.4) into the midget impinger, using a graduated cylinder to measure the volume.

8.8.4 Connect the impinger (via the absorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.8.5 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and / or volume as accurately as possible. The sample should be taken at a flow rate of 2.5 lpm. A sample size of not more than 200 litres and no less than 10 litres should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 0.2 mg/m^3 (760 mm Hg, 25°C).

8.8.6 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1 to 2 ml) of unused absorbing solution and add the wash to the impinger. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e. taped) to secure the top tightly.

8.8.7 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis can not be done within a day.

8.8.8 Whenever possible, hand delivery of the samples is recommended.

8.8.9 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.8.10 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled as the other samples (seal and transport) except that no air is sampled through, and this labled as a blank.

8.9.0 Analysis of Samples

8.9.1 Transfer the sample from the impinger to a 50 ml plastic beaker, add 10ml TISAB and dilute to 25 ml with double distilled water. Stir the solution.

8.9.2 The fluoride ion electrode and the reference electrode are lowered into the stirred solution and the resulting mV reading recorded (to the nearest 0.5 millivolt) after it has stabilized (drift less than 0.5 mV per min).

8.10.0 Calibration and Standards

Prepare a series of fluoride standard solutions by diluting 5 ml of each fluoride standard (8.7.10) and 5 ml TISAB in a clear polyethylene beaker to 25 ml with double distilled water. Insert the fluoride ion electrode and the reference electrode into each of the stirred calibration solutions starting with the most dilute solution and record the resulting mV reading to the nearest 0.5 mV. Plot the mV readings vs the fluoride ion conc of the standard on semi-log paper. The fluoride ion conc in µg/ml is plotted on the log axis. The calibration points should be repeated twice daily.

8.11.0 Calculations

8.11.1 The conc (µg/ml) of fluoride in the sample solution is obtained from the calibration curve.

8.11.2 Total µg F^- in the sample = sample conc (µg/ml) x sample solution volume (ml).

8.11.3 The total µg F^- is divided by the volume in litres, of air sampled to obtain conc in µg F^-/litre or mg F^-/m^3.

$$\text{mg } F^-/m^3 = \mu g\ F^-/\text{litre} \quad \text{or} \quad \text{mg } F^-/m^3 = \frac{\text{total } \mu g\ F^-}{V_s}$$

(Section 8.11.4)

8.11.4 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V_x \frac{P_{bar}}{760} \times \frac{298}{T+273}$$

where

V_s = Volume of air in litres at 25°C and 760 mm Hg

V = Volume of air in litres as measured

P_{bar} = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

8.11.5 The conc can also be expressed in ppm, defined as µl of component per litre of air.

$$\text{ppm } F^- = \mu l\ F^-/V_s = \frac{24.45}{MW} \times \mu g\ F^-/V_s = 1.29\ \mu l\ F^-/V_s$$

where

24.45 = Molar volume at 25°C and 760 mm Hg

MW = 19, weight of fluoride ion, (i.e., 19 ug F^- = 24.45ul at 25°C, 760 mm Hg)

8.11.6 To calculate the conc of hydrogen fluoride as mg HF/m^3 or ppm HF, simply multiply the corresponding concentration of F^- (from 8.11.3 or 8.11.4) by 1.05