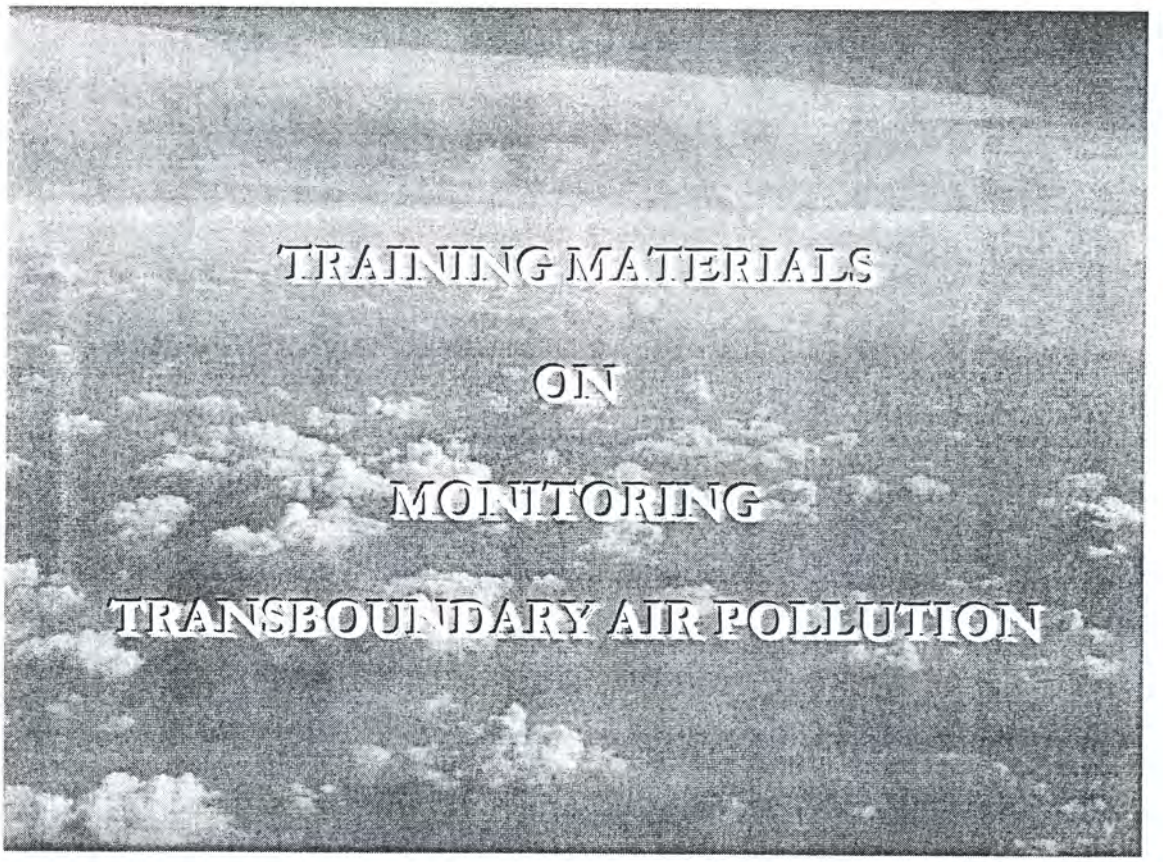
Malé Declaration on Control and Prevention of Air Pollution and Its Likely Transboundary Effects for South Asia



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Contributors to this training material

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Chapter 1

Units and Materials and Energy Balances

1 Units of measurement

In any environmental management programme measurement, accounting and balancing of materials, pollutants or otherwise, is required. For example, in a sodium hydroxide manufacturing industry, which may use mercury in its process, it is important to know the amounts of mercury purchased every year and discharged in gaseous, liquid and solid wastes and that carried over in the product. This will enable designing of a suitable environmental monitoring and management programme. It is therefore necessary to follow a commonly used and accepted system of measurements consistently. This session reviews some basic considerations which an environmental scientist or engineer must be familiar with. to carry out such accounting.

Table 1 gives some of the common units that are used in environmental management calculations. It also gives conversion factors between the International System of Units (SI) and British System, commonly known as foot pound second system (fps). In most countries measurements are made in units based on SI units.

Table 1: Some basic units and conversion factors.

Quality	SI units	SI Symbol	Multiple by	To obtain fps units
Length	meter	m	3.2808	ft
Mass	kilogram	kg	2.2046	lb
Temperature	celsius.	°C	1.8 +32	°F
Area	square meter	m^2	10.7639	ft^2
Volume	cubic meter	m^3	35.314	ft^3
Energy	kilojoule	kJ	0.9478	Btu
Power	watt	W	3.4121	Btu/h
Velocity	meter/second	m/s	2.2369	mi/h
Flow rate	$meter^3$/second	m^3/s	35.3147	ft^3/s
Density	kilogram/$meter^3$	kg/m^3	0.06243	lb/ft^3

In the environmental field, it is quite common to encounter both extremely large quantities and extremely small ones. To describe such extreme values a system of prefixes are used with the units. Commonly used prefixes and their meaning are presented in Table2.

Table2: **Common prefixes**

Prefix	Symbol	Meaning
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
deca	da	10
hecta	h	10^{2}
kilo	k	10^{3}
mega	M	10^{6}

Commonly used units of length, area, volume and mass are:

1	kilometer (km)	=	1000m
1	m	=	100 centimeter (mm)
1	cm	=	10 millimeter (mm)
1	hectare	=	10,000 m^2
1	liter (L)	=	1000 mL=1000 cm^3
1	m^3	=	100 L=1kL
1	kg	=	1000 gram (g)
1	g	=	1000 milligram (mg)
1	mg	=	1000 micro gram (μg)

Units of Concentration

Concentration of pollutants in water or air are expressed as a ratio: mass or volume of pollutant in a given mass or volume of water or air. Substances in water are usually expressed in terms of mass of substance per unit volume of the mixture such as mg/L or μg/L.

Example 1

4 kg of common salt is thrown in a pond containing $800m^3$ water-What is the resulting concentration of the salt in the water in mg/L, µg/L?

Solution

$$\frac{4kg}{800m^3} \times \frac{10^6\ mg}{1\ kg} \times \frac{1m^3}{10^3 L} = 5\ mg/L$$

$$\frac{5mg}{L} \times \frac{1000\ \mu g}{1\ mg} = 5{,}000\ \mu g/L$$

Concentration of substances in liquids are also expressed as ratio of mass of the substance to a specified mass of mixture, usually as parts per million (ppm by weight). Since most concentrations of pollutants in water are small, one liter of mixture weighs essentially 1000g, we can write:

$$\frac{1mg}{L} \times \frac{IL}{1000g} \times \frac{1g}{1000mg} = 1\ mg/10^6\ mg = 1ppm$$

Therefore mg/L and ppm may be used interchangeably as long as the liquid density can be assured to be 1000 g/L.

Sometimes concentrations in liquids are also expressed in percentage (mass/mass)

Example 2

For the data of Example 1, calculate the concentration in percentage. Assume the density of solution as 1000 kg/m^3 (or 1000 g/L)

Solution

$$\frac{4kg}{800m^3} \times \frac{1m^3}{1000\ kg} \times 100 = 0.0005\%$$

Note: ppm can be changed to percent by dividing by 10^4.

Concentration of air pollutants are measured both in terms of mass of pollutant (µg or mg) per unit volume (m^3) of the mixture and as percent or ppm by volume. Since the volume of a gas changes significantly with temperature and pressure, to calculate volume at different temperature and pressure help is taken of the relationship.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Where P= pressure, V= volume, T=Temperature in degree Kelvin (°K) and subscripts 1 and 2 correspond to the changes in the condition of measurement.

Example 3

14 g sulphur is burnt in a room having 5000 m^3 air maintained at 15°C Calculate resulting sulphur dioxide concentration in the air in the room in $\mu g/m^3$, ppm and percent by volume.

Solution

Calculate the volume of 5000 m3 air at one atm. pressure at 25°C and 0°C, using $V_1=V_2$. T_1/T_2

$$V_{25} = \frac{5000\ (273 + 245)}{(273 + 15)} = 5173.6\ m^3$$

$$V_0 = \frac{5000\ (273 + 0)}{(273 + 15)} = 4739.6\ m^3$$

Calculate the mass and volume of SO_2 produced at 0 °C from stochiometric equation.

$$S + 0_2 = SO_2$$

$$\text{Mass of } S0_2 \text{ produced} = 14\ g\ S \times \frac{64g\ S02}{32\ g\ S} = 28\ g$$

Since 1g mole of a gas occupies 22.4 L at STP

$$\text{Volume of } SO_2 \text{ produced at 0C} = \frac{28\ g\ S0_2}{64\ g\ S0_2/mole} \times \frac{22.4\ L\ S0_2}{1\ mole} = 9.8\ L$$

$$\frac{28\ g\ S0_2}{5173.6\ m^3\ air} \times \frac{10^6\ \mu g}{1\ g} = 5412\ \mu g/m^3 \text{ at } 25^\circ C$$

and $$\frac{9.8\ L}{47.39.6\ m^3} \times \frac{1\ m^3}{10^3\ L} \times 106 = 2.06\ ppm$$

and $$\frac{2.06}{10^4} = 0.0002\ \%$$

Note: $mg/m^3 = \frac{ppm \times mol\ wt}{24.45}$ (at 25 °C and 1 atm)

For uniformity in reporting, the concentration of air pollutants is usually reported as $\mu g/m^3$ at 25°C. This is also written as $\mu g/Nm^3$ (microgram per normal meter cube).

2 Materials and energy balance

The first step in understanding a process is to compile an overall materials and energy balance. This step alone may locate imbalances and inconsistencies. It may not be possible to measure every flowing stream in a process. Careful measurement of all inputs and outputs can characterize the unknown streams. Such balances can also give an idea of the behaviour of a system if any of the input and output conditions are modified. Lastly and most importantly materials and energy balances can give us important information regarding the impact on the environment of a proposed new plant or activity. These aspects are illustrated by the following examples.

Example 4

A high volume sampler filtered air at an average rate of 1.2 m^3/min for 24th period. This resulted in collection of 0.85 g of dust particles. What is the particulate concentration?

Solution

Total air filtered = 1.2 m^3/min x60 min/h x 24 =1728m^3

Particulate concentration = 0.85g/1728 m^3 x 10^6 µg/g

= 491 $\mu g/m^3$

Example 5

A bag house is being used to remove dust from an air exhaust stream flowing at 100.0 m^3/min. The dirty air contains 15.0 g/m^3 of particles, while the cleaned air from the bag house contains 0.020 g/m^3. The industry's operating permit allows the exhaust stream to contain as much as 0.90 g/m^3. For various operating reasons, the industry wishes to bypass some of the dirty air around the bag house and blend it back into the cleaned air so that the total exhaust stream meets the permissible limit. Assume no air leakage and negligible change in pressure or temperature of the air throughout the process. Calculate the flow rate of air through the bag house and the mass of dust collected per day (in kg).

Solution

Draw a flow diagram of the process as shown in Figure 1. In this problem two balances can be made, namely, flow rate of dust in g/min and flow rate of air in m3/min. Balancing of flow rate of air in m^3/min is possible because the temperature and pressure of air remains constant in the system.

Write a balance for dust around the total system:

Input = Output from bag house +Output in the mixed exhaust

Or Output from bag house = 100m^3/min. x 15 g/$m^3$100m^3/min. x 0.90 g/m^3 = 1410 g/min.

Or Daily dust Output = 2030 kg

Write a balance for airflow around A:
100 = X+Y, where X and Yare bypass stream and flow through baghouse, respectively.

Write a balance for dust around B:
15x + 0.02y = 0.9x100
Solving the last two equations
X, the bypass stream = 5.9 m^3/ min.
Y, the flow through bag house = 94.1 m^3/min.

Example 6

A 150 MW coal-fired power plant is 40 percent efficient. If the coal contains 42 percent ash and 0.5 percent sulphur, calculate the amount of ash and SO_2 produced per day. Assume calorific value of coal = 6,000 kJ/kg coal.

Solution

First we determine the input rate of heat to the plant. Since it is 40% efficient, heat required

$$\frac{150 \times 103\ kW}{0.4} = 375000\ kW = 375000\ kJ/s.$$

$$\text{Therefore coal used} = \frac{37500\ kJ}{S} \times \frac{1\ kg\ coal}{6000\ kJ}$$

$$\times \frac{3600s}{1h} \times \frac{24h}{1d} \times \frac{1T}{1000kg} = 5400\ T/d$$

Since the coal is 42% ash, amount of ash produced 5400 x 0.42 = 2269 T/d

Usually only 10 percent of the ash is collected as, bottom ash. The balance escapes with flue gas as fly ash. Therefore the plant will emit 0.9 x 2268= 2041 T/d ash if no ash removal method is adopted.

If an electrostatic precipitator (ESP) of 97% efficiency is installed, the plant will emit 0.3 x 2268=6.8 T/d ash.

Amount of SO_2 can be calculated from stochiometric relation: $S + O_2 = SO_2$, i.e., 32 g S produces 64g SO_2.

$$\text{Therefore SO2 produced} = \frac{5400\ T\ Coal}{D} \times \frac{0.5Gs}{100g} \times \frac{64g\ SO2}{32g\ S} = 54\ T/d$$

Note: 1W = 1 J/s

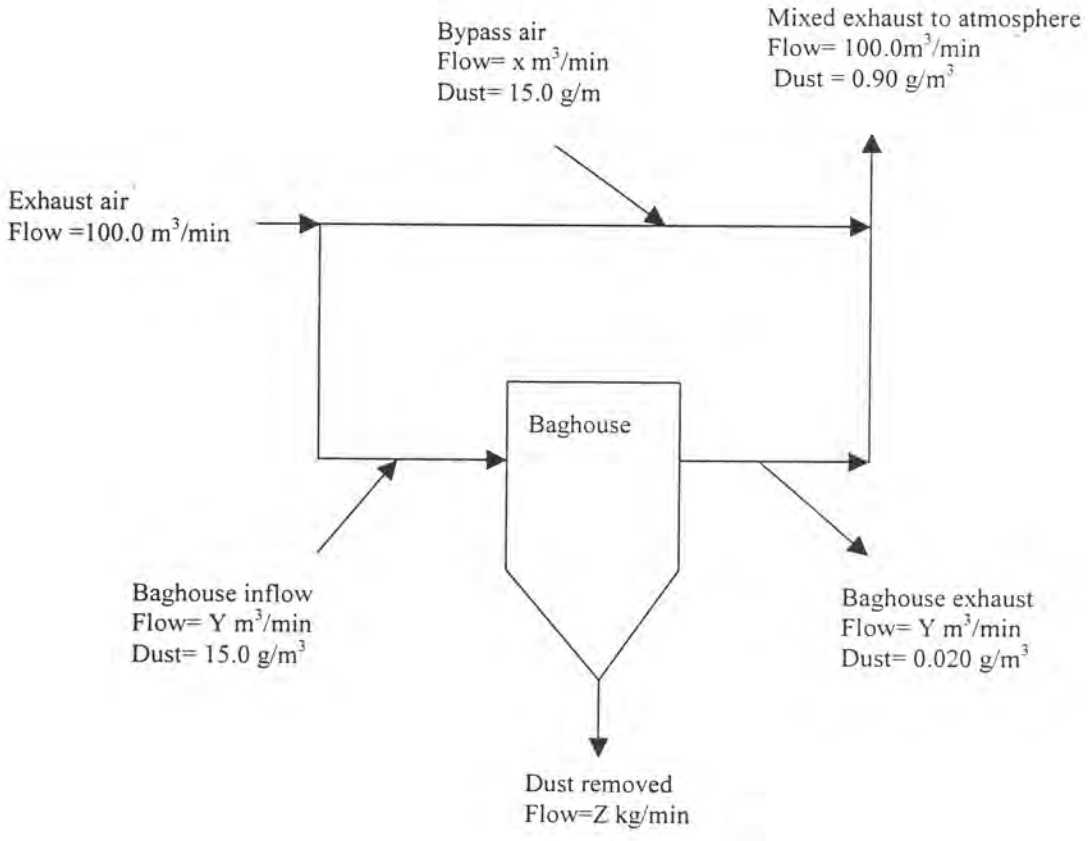

FIGURE 1 PROCESS DIAGRAM FOR THE BAGHOUSE EXAMPLE.

Chapter 2
Air Pollution, Sources and Characteristics

1 Introduction

Air pollution is the presence of substances in air in sufficient concentration and for sufficient time, so as to be, or threaten to be injurious to human, plant or animal life, or to property, or which reasonably interferes with the comfortable enjoyment of life and property.

Air pollutants arise from both man made and natural processes. Pollutants are also defined as *primary pollutants* resulting from combustion of fuels and industrial operations and *secondary pollutants,* those which are produced due to reaction of primary pollutants in the atmosphere. The ambient air quality may be defined by the concentration of a set of pollutants which may be present in the ambient air we breath in. These pollutants may be called *criteria pollutants. Emission standards* express the allowable concentrations of a contaminant at the point of discharge before any mixing with the surrounding air.

Table 1 lists names of some common air pollutants, their sources and classification. This session will be limited to discussion of primary pollutants generated due to human activity.

Table 1: Common pollutants and their sources.

Pollutants	Sources
Suspended particulate Matter, SPM[a]	Automobile, power plants, boilers, Industries requiring crushing and grinding such as quarry, cement.
Chlorine	Cholr-alkali plants.
Fluoride	Fertilizer, aluminum refining
Sulphur dioxidea	Power Plants, boilers, sulphuric acid manufacture, ore refining, petroleum refining.
Lead	Ore refining, battery manufacturing, automobiles.
Oxides of nitrogen,[a] NO, NO_2 (NO_X)	Automobiles, power plants, nitric acid manufacture, also a secondary pollutant
Peroxyacetyl nitrate, PAN	Secondary pollutant

Formaldehyde	Secondary pollutant
Ozone[a]	Secondary pollutant
Carbon monoxide[a]	Automobiles
Hydrogen sulphide	Pulp and paper, petroleum refining.
Hydrocarbons	Automobiles, petroleum refining
Ammonia	Fertilizer plant

a- Criteria pollutants

2 Combustion sources

By combustion sources is meant operations where primarily fossil fuels, coal, natural gas, petrol, diesel and furnace oil are burnt to obtain energy. This includes power plants, industrial boilors, domestic heating and automobiles.

Thermal power pants

Thermal power plants are major sources of SPM, $S0_2$ and NO_x. Depending upon the type of fuel used, emission of one or more of these pollutants may be of environmental-significance.

A Large amount of SPM as fly ash is emitted from coal fired plants, particularly if the ash content of coal is high and a fly ash removal unit, such as, an electrostatic precipitation (ESP) is not used.

Oxides of nitrogen formed in combustion processes are usually due either to thermal fixation of atmospheric nitrogen in combustion air or to the conversion of chemically bound nitrogen in the fuel. Thermal fixation occurs when combustion temperature is above 1600°C. For natural gas and distillate oil nearly all NO results from thermal fixation. For residue oil and coal, the contribution to NO emission from fuel bound nitrogen may be significant.

The concentration of NO_x formed increases with increase in excess oxygen maintained in the combustion process and with the increase in temperature of the furnace. For coal based thermal power plants in. India, it ranges between 100 and 200 mg/Nm3 in the flue gas. In the case of natural gas and liquid fuels, the emission limits for flue gases prescribed in European countries is in the range of 200 - 400 mg/Nm3.

Example 1

Calculate S02 concentration in flue gas when one mole of C7H13 containing 1 % sulphur is burnt in presence of stochiometric amount of oxygen.

Solution

First we write stochiometric equation for combustion:

$$C_7H_{13} + 1\ 0.25O_2 = 7\ CO_2 + 6.5\ H_2O$$

Since O_2 is supplied through air which also contains nitrogen and in air each mole of oxygen is accompanied by 3.76 mole N_2, for 10.25 mole O_2, 38.54 N_2 will be supplied. Therefore we may write.

$$C_7H_{13} + 1\ 0.25O_2 + 38.54\ N_2 = 7\ CO_2 + 6.5\ H_2O + 38.54N_2$$

Therefore quantity of flue gas at STP = 45.54 mole

$$\text{or } 45.54 \text{ mole} \times \frac{22.4 \text{ L}}{1 \text{ mole}} = 1020 \text{ L}$$

Since one mole C_7H_{13} = 7 x 12 + 13 x 1 = 97 g, sulfur contents of fuel = 97 x 0.01 == 0.97 g. Therefore S02 produced = 1.94 g or 1940 mg/mole of fuel.

As an approximation, neglecting the volume of oxygen consumed in production of $S0_2$, concentration of SO_2 = 1940 mg/1020 L = 1902 mg/m^3, at STP.

$$\text{or } 1902 \times \frac{273}{298} = 1742 \text{ mg/Nm}^3$$

Automobiles

In urban areas automobiles form a significant source of a number of air pollutants, namely, particulates, NO_x, hydrocarbons, carbon monoxide and lead- These pollutants are produced when fuel is burnt under less than ideal conditions. Non-uniform oxygen supply within the combustion chamber and lower flame temperature leads to incomplete combustion releasing CO, HC and unburnt particles in the exhaust.

Tetraethyl lead, $(C_2H_5)_4$ Pb, is added to petrol as anti-knock additive. Where such petrol is used lead is emitted in the exhaust fumes as inorganic particulates.

3 Industrial sources

Only two sources are discussed here as illustrative examples.

Cement manufacture

Raw materials include lime, silica, aluminum and iron. Lime is obtained from calcium carbonate. Other raw materials are introduced as sand, clay, shale, iron are and blast furnace slag. The process consist of mining, crushing, grinding, and calcining in a long cylindrically shaped oven or kiln. Air pollutants can originate at several operations as listed below.

Source	Emission
o Raw material crushing, grinding	Particulates
o Kiln operation and. Cooling	Particulates, CO, SO_2 , NO_x, HC
o Product grinding and packaging	Particulates

Control of emission of particulate matter is economically viable as the cost of collected dust (raw material and product) pays for control measures.

Sulphuric acid manufacture

Sulphuric acid is produced from sulphur, which is burnt to obtain SO_2. Sulphur dioxide is converted to trioxide in presence of vanadium pentaoxide catalyst. The sulphur trioxide is absorbed in recycling concentrated sulfuric acid. Unreacted SO_2 escapes with the flue gas. New large plants now a days use double conversion double absorption (DCDA) process realizing above 99 percent efficiency.

Example 2

A 250 T/d DCDA sulphuric acid plant burns 82T/d sulphur in the manufacturing process. Flue gas containing 350 ppm SO_2 is discharged at the rate of 35 Nm^3/s, What is the percent recovery of sulfur in the product.

Solution

$$350 \text{ ppm } SO_2 = \frac{350 \times 64}{24.45} = 916 \text{ mg/Nm}^3$$

Therefore SO2 discharged with flue gas

$$= \frac{916}{Nm^3} \times \frac{35Nm^3}{s} \times \frac{3600s}{1h} \times \frac{24h}{1d} \times \frac{1kg}{10^6mg} \times \frac{1T}{10^3kg} = 2.77 \text{ T/d}$$

The quantity of sulphur in 2.77 T/d SO2

$$= \frac{2.77 \text{ T}}{d} \times \frac{32 \text{ g S}}{64 \text{ g } SO_2} = 1.35 \text{ T/d}$$

$$\text{Therefore sulphur recovery} = \frac{82 - 1.38}{82} = 98.3 \%$$

Note: DCDA plants are expected to give better than 99% recovery. Therefore the reason for poor performance should be investigated and corrected.

4 Characteristics

Major effects of some of the common pollutants are described in this section.

Suspended particulate matter

Atmospheric particulate matter is defined to be any dispersed matter, solid or liquied, smaller than, 500 µm. Under various conditions of their generation, they are also called by other names such as *dust, fume, smoke and mist.* Dust usually refers to particles in the range of 1 to 200 µm size. Fume is very fine solid or liquid particles arising from chemical reactions or condensation of gases. Smoke refers to finely divided particles resulting from incomplete combustion of substances such as coal, petroleum, etc.

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Particles in the range of 0.1 to 10 are of, most interest from health viewpoint. Particulate matter of less then 10 μm size (PM_{10}) is classified as respirable dust. Larger particles that enter the respiratory system are trapped by hairs and lining of nose or can be captured by mucus in upper respiratory tract and worked back to the throat by cilia and removed by spitting, Figure 1.

Particles between 0.5 and 10 μm, called thoracic particles, penetrate to the lungs and are deposited there. These particles by themselves and or by carrying other air pollutants adsorbed on them may cause the greatest harm. Elevated particulate concentrations in the atmosphere, in the range of 400 $\mu g/m^3$ and above especially in conjunction with oxides of sulphur have been linked to respiratory infections, bronchitis, asthma, pneumonia and the like. Many carbonaceous particles, especially those containing polycyclic aromatic hydrocarbons (PAH) are suspected carcinogens.

Sulphur dioxide

Sulphur dioxide when released in the atmosphere can also convert to SO_3, which leads to production of sulphuric acid. When SO_3 is inhaled it is likely to be absorbed in moist passages of respiratory tract. When it is entrained in an aerosol, however, it may reach far deeper into the lungs.

Figure 2 summarizes adverse health effects of SO_2. Sulphur dioxide can damage vegetation and cause corrosion. Airborne sulfates reduce visibility. It is also the cause of acid rain in some countries.

Nitrogen oxides

Almost all NO_x emissions are in the form of NO, which has no known adverse health effects in the concentrations found in atmosphere. However, NO can be oxidized to NO_2 in the atmosphere, which in turn may give rise to secondary pollutants, which are injurious. NO_2 may also lead to formation of HNO_3, which is washed out of the atmosphere as acid rain.

Carbon monoxide

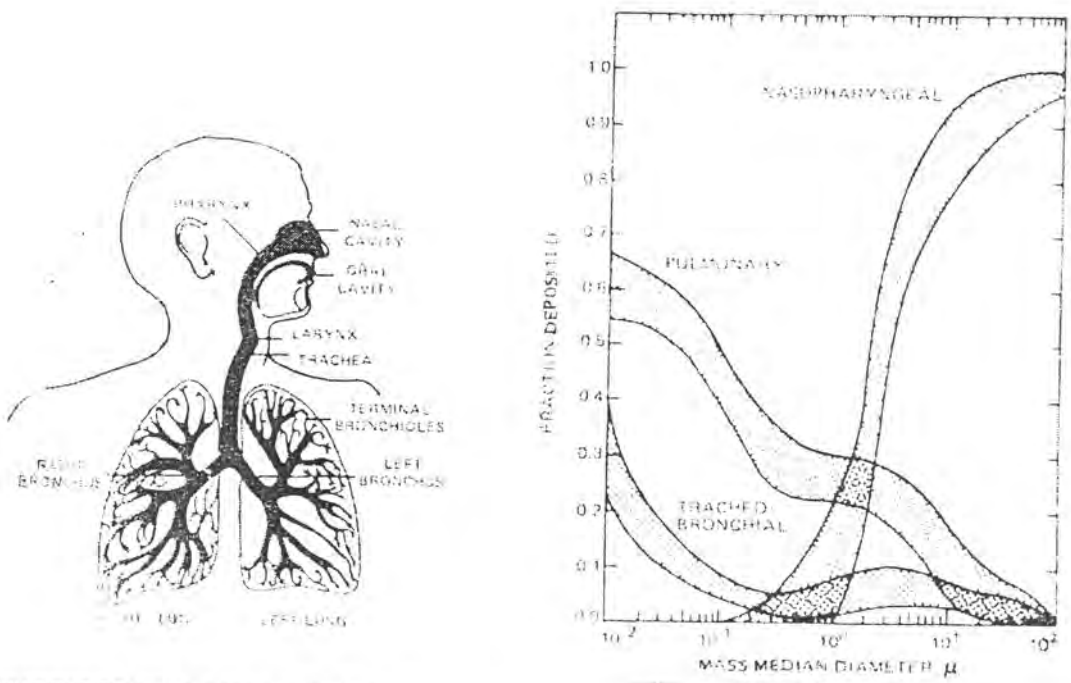
Most of the CO emissions are from transportation sector. Peak concentrations occur at street level in busy urban centers particularly when there is no atmospheric mixing as it happens during winter season. Carbon monoxide interferes with blood's ability to carry oxygen. With the blood stream carrying less oxygen, brain function is affected and heart rate increases in an attempt to offset

the oxygen deficit. Breathing between 20 to 35 ppm CO in air for 4 h results in impairment of time related response. Individuals with heart condition may experience chest pain. Exposure to 100 ppm concentration would result in dizziness.

Lead

Lead released from motor vehicle exhaust may affect human populations by direct inhalation, in which case people living nearest to highways are at greatest risk. Lead can be ingested also after it is deposited on to foodstuffs.

Measurements made in exposed communities indicate that lead concentration of 1 $\mu g/m^3$ in ambient air results in an increase of about 1-2 µg per decilitre (µg/dl) in blood. Lead poisoning can cause destructive behavioural changes, learning disabilities and permanent brain damage. Children and pregnant women are at greatest risk. Blood levels of 50 – 60 µg/dl are associated with neurobehavioural changes in children.



DIVISIONS OF HUMAN RESPIRATORY TRACT: NASOPHARYNGEAL, TRACHEOBRONCHIAL, PULMONARY

FIGURE 1 DEPOSITION OF SPM IN HUMAN RESPIRATORY SYSTEM.

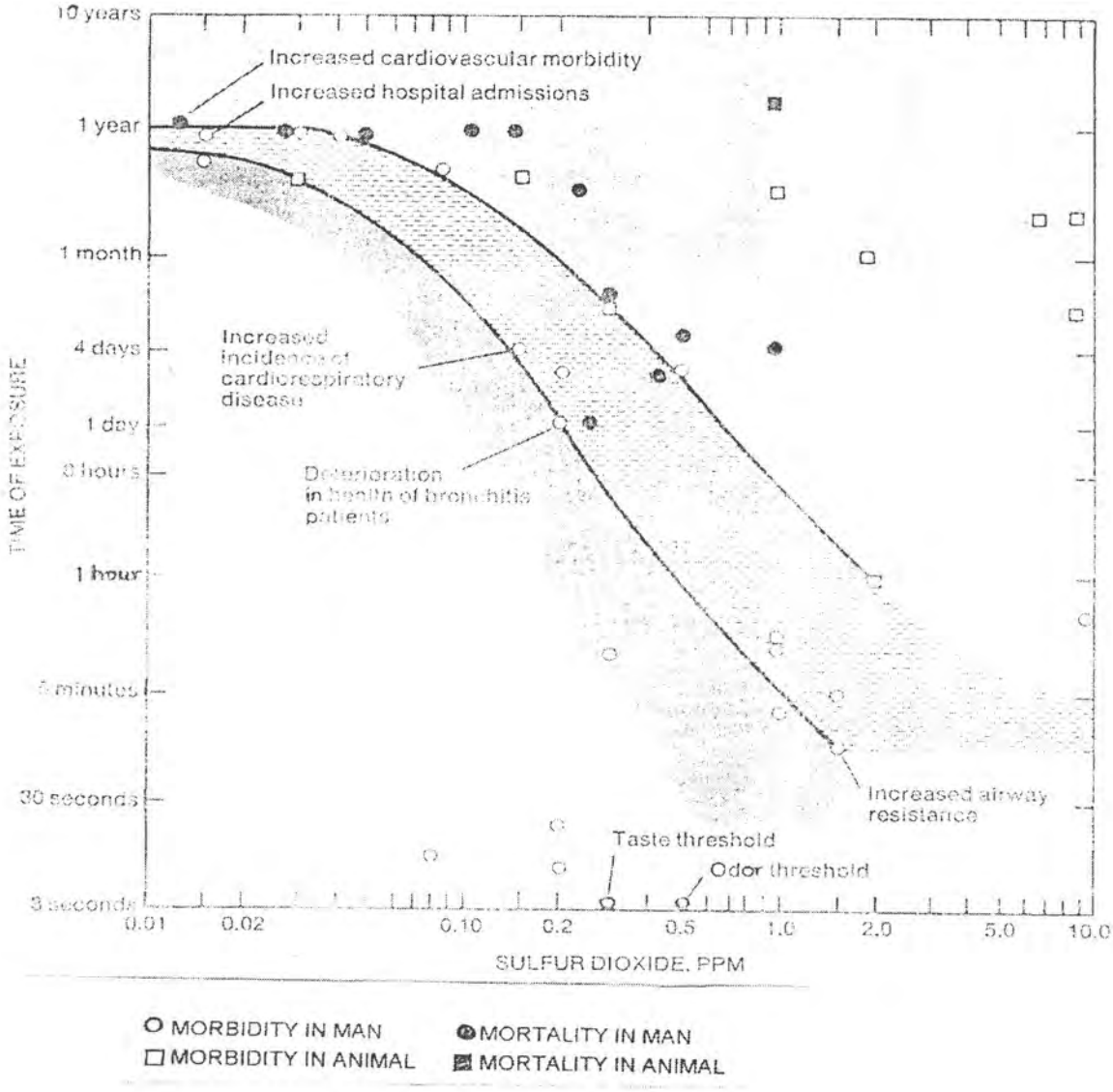


FIGURE 2 EFFECTS OF SULPHUR DIOXIDE ON HEALTH.

Chapter 3
Air Pollution and Meteorology

The science of meteorology has great hearing on air pollution. An air pollution problem involves three parts: the source, the movement of the pollutant and the recipient. All meteorological phenomena are a result of interaction of the elemental properties of the atmosphere, heat, pressure, wind and moisture. In this lecture we will discuss the meteorological conditions, which directly influence the transport and dispersion of pollutants.

1 Wind

Wind is simply air in motion. On global or macroscale wind patterns are set up due to unequal heating of earth surface by solar radiation at the equator and the polar regions, rotation of the earth and the difference between conductive capacities of land and ocean masses. Secondary or mesoscale circulation patterns develop because of the regional or local topography. Mountain ranges, cloud cover, waterbodies, deserts, forestation, etc., influence wind patterns on scales of a few hundred kilometers. Accordingly a pattern of wind is setup, some seasonal and some permanent.

Microscale phenomenon occurs over areas of less than 10 km extent. Standard wind patterns may deviate markedly due to varying frictional effects of the earth surface, such as, rural open land, irregular topography and urban development, effect of radiant heat from deserts and cities, effect of lakes, etc.

The movement of air at the mesoscale and microscale levels is of concern in control of air pollution. A study of air movement over relatively small geographical regions can help in understanding the movement of pollutants.

The variation of the horizontal wind speed with height is important in evaluating diffusion from stacks. Close to the ground the effects of friction retard the wind flow and cause it to change the direction as well. Figure 1 illustrates these effects. In the upper layers, 200 m to 500 m above ground, the wind speed reaches the maximum value.

It is obviously important in predicting pollutant dispersion to know the direction of wind. The wind direction and speed data may be collected every hour in a month and classified according to speed and direction. It is then summarized in the form of a polar diagram called *wind rose*. Figure 2 shows a hypothetical wind rose. The position of the spokes show the direction from which the wind was blowing, the length of various segments of the spokes show the percent of time the wind was of the designated speed. Thus from the diagram, most often (12% of time) the wind was from SE; the strongest wind (9-11 m/s) was from NW and NNW.

2 Lapse rate

As a parcel of air rises in the earth's atmosphere it experiences lower and lower pressure from the surrounding air molecules, and thus it expands. This expansion lowers its temperature. Ideally, if it does not absorb heat from its surroundings and it does not contain any moisture, it cools at a rate of 1°C/100 m rise. This is known as *dry adiabatic lapse rate.* If the parcel moves down it warms up at the same rate.

For a particular place at a particular time, the existing temperature can be determined by sending up a balloon equipped with a thermometer. The balloon moves through the air, and not with it. The temperature profile of the air, which the balloon measures, is called the *ambient lapse rate, environmental lapse rate,* or the *prevailing lapse rate.*

A super-adiabatic lapse rate also called a strong lapse rate occurs when the atmosphere temperature drops more than 1°C/100m. A sub-adiabatic rate also called weak lapse rate, is characterized by drop of less than 1°C/100 m.

A special case of weak lapse rate is the inversion, a condition which has warmer layer above colder air.

During super-adiabatic lapse rate the atmospheric conditions are unstable. This is illustrated in Figure 3 (a). If a parcel of air at 500m elevation, at 20°C is pushed upward to 1000m, its temperature will come down to 15°C
(according to adiabatic lapse rate). The prevailing temparature is however 10°C at 1000m. The parcel of air will be surrounded by colder air and therefore will keep moving up. Similarly if the parcel is displaced downwords, it will become colder than its surroundings and therefore will move down. Superadiabatic conditions are thus unstable, characterized by a great deal of vertical air movement and turbulence.

The sub-adiabatic condition shown in Figure 3.1 (b) is by contrast a very stable system. Consider again a parcel of air at 500 m elevation at 20°C. If the parcel is displaced to 1000 m it will cool by 5°C to 15°C. But the surrounding air would be warmer. It will therefore fall back to its point of origin. Similarly if a parcel of air at 500 m is pushed down, it will become warmer than its surrounding and therefore will rise back to its original position. Thus such systems are characterized by very limited vertical mixing.

3 Inversion

An inversion is an extreme sub-adiabatic condition, and thus the vertical air movement within the inversion is almost nill. The two most common kind of inversion are *subsidence inversion* and *radiation inversion.* These are illustrated in Figure 4.

The base of the subsidence inversion lies some distance above earth's surface. This type of inversion is formed due to adiabatic compression and warming of sinking air mass to a lower altitude in the region of a high pressure center.
In the case of radiation inversion, the surface layers of the atmosphere during the day receive heat by conduction, correction and radiation from the earth's surface and are warmed. This results in a temperature profile in the lower atmosphere which is represented

by a negative temperature gradient. On a clear night, th. ground surface radiates heat and quickly cools. The air layer adjacent to the earth surface are cooled to a temperature below that of the layers of air at higher elevations. This type of the inversion is strongest just before daylight when it may extend to 500 m. It break up as the morning sun heats the ground.

4 Maximum mixing depth

The dispersion of pollutants in the lower atmosphere is greatly aided by the convective and turbulent mixing that takes place. The vertical extent to which this mixing takes place depends on the environmental lapse rate which varies diurnally, from season to season and is also affected by topographical features. The depth of the convective mixing layer in which vertical movement of pollutants is possible, is called the maximum mixing depth (MMD).

Figure 5 illustrates these MMDs for different lapse rate profiles. These profiles are usually measured at night or early in the morning. An air parcel at a temperature (maximum surface temperature for the month) warmer than the existing ground level temperature rises and cools according to adiabatic lapse rate. The level where its temperature becomes equal to the surrounding air gives the MMD value. Urban air pollution episodes are known to occur when MMD is 1500 m or less.

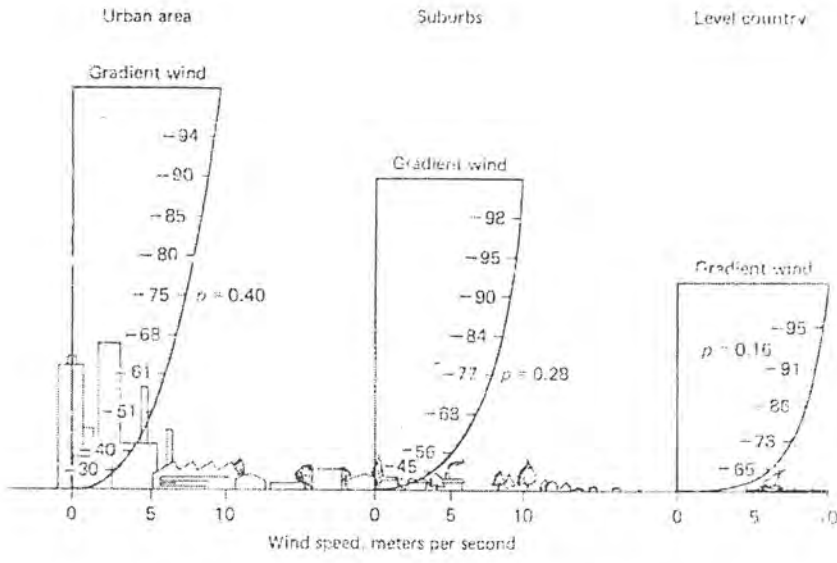


FIGURE 1 EFFECT OF TERRAIN ROUGHNESS ON WIND PROFILE.

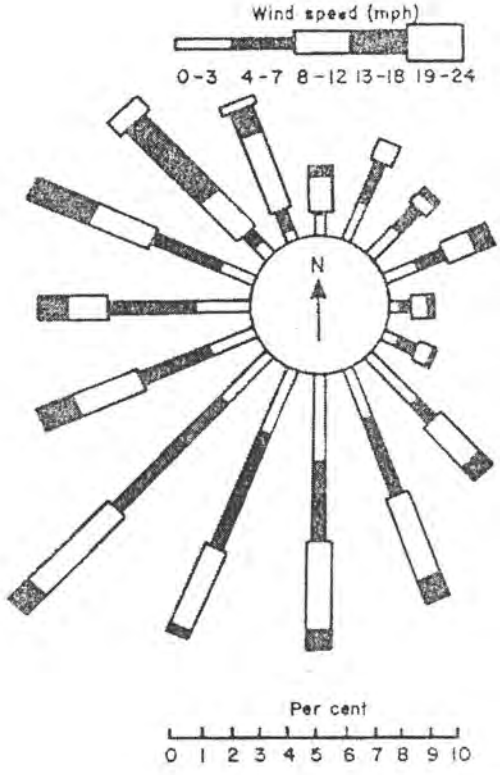
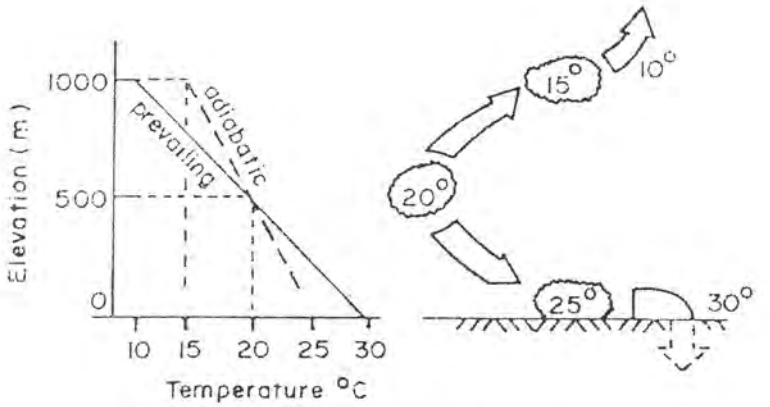
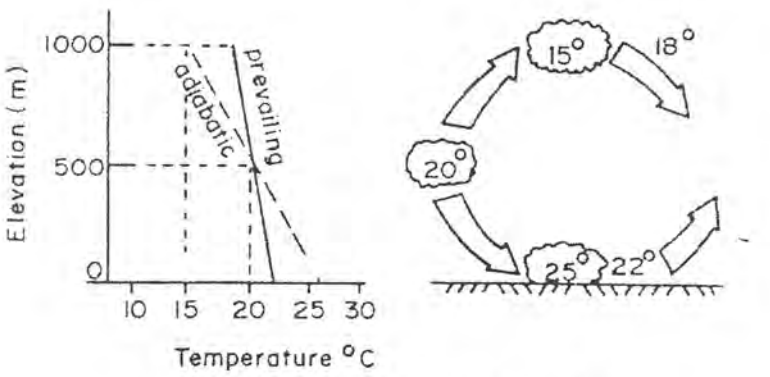


FIGURE 2 TYPICAL WIND ROSE.



A. Superadiabatic conditions (unstable)



B. Subadiabatic conditions (stable)

FIGURE 3 STABILTY AND VERTICAL AIR MOVEMENT.

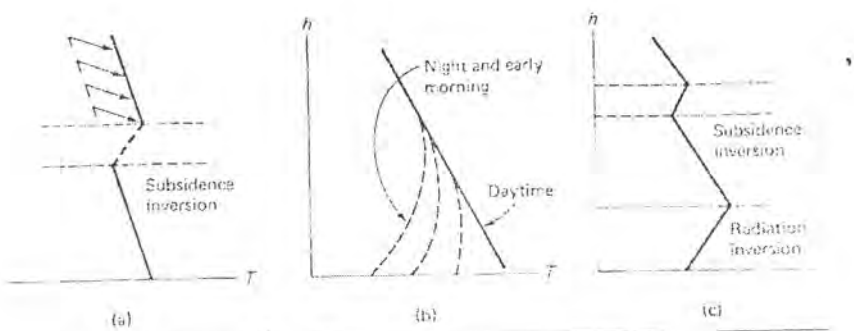


FIGURE 4 ILLUSTRATIONS OF SUBSIDENCE AND RADIATION INVERSIONS.

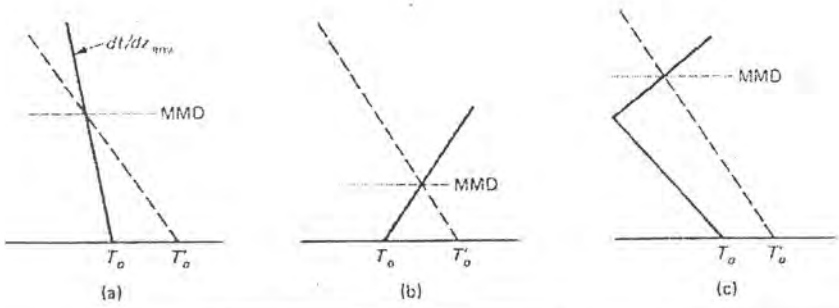


FIGURE 5 MAXIMUM MIXING DEPTH (MMD) UNDER VARIOUS ATMOSPHERIC CONDITIONS, (ADIABATIC PROFILE ------, ENVIRONMENTAL PROFILE———).

Chapter 4
Dispersion of Pollutants

1 Dispersion characteristics of stack plumes

Dispersion is the process of spreading out pollution emission over a large area and thus reducing their concentration. Wind speed and environmental lapse rates directly influence the dispersion pattern. Five classifications of plume behaviour, which may occur under some commonly encountered metrological conditions, are shown in Figure 1 (a) to (e) and discussed in the following sections.

Coning

A *coning* plume, shown in Figure 1 (a), occurs under essentially neutral stability, when environmental lapse rate is equal to adiabatic lapse rate, and moderate to strong winds occur. The plume enlarges in the shape of a cone. A major part of pollution may be carried fairly far downwind before reaching ground.

Looping

Under super-adiabatic condition, both upward and downward movement of the plume is possible. Large eddies of a strong wind cause a *looping* pattern, Figure 1 (b). Although the large eddies tend to disperse pollutants over a wide region, high ground level concentrations may occur close to the stack.

Fanning

A *fanning* plume occurs in the presence of a negative lapse rate when vertical dispersion is restricted, Figure 1 (c). The pollutants disperse at the stack height, horizontally in the from of a fanning plume.

Fumigation

As shown in Figure 1 (d), when the emission from the stack is under an inversion layer, the movement of the pollutants in the upward direction is restricted. The pollutants move downwards. The resulting *fumigation* can lead to a high ground level concentration downwind of the stack.

Lofting

When the stack is sufficiently high and the emission is above an inversion layer, Figure 1 (e), mixing in the upward direction is uninhibited, but downward motion is restricted. Such *lofting* plumes do not result in any significant concentration at ground level. However, the

pollutants are carried hundreds of kilometers from the source.

2 Stability Classification

For the purpose of calculation of concentration of pollutants downwind of a source the stability of the atmosphere is classified as :

A= Extremely unstable, B= Moderately unstable, C= Slightly unstable, D= Neutral, E= Slightly stable, F= Stable

These classifications are arrived at from metrological condition of wind speed, solar insulation and cloudiness, given in Table 1.

Table 1. Atmospheric stability classification

Surface[a]	Day solar insolation			Night cloudiness	
Wind, m/s	Strong[b]	Moderate[c]	Slight[d]	Cloudy > 4/8	Clear <3/8
<2	A	A-B	B	E	F
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	E
>6	C	D	D	D	D

a- at 10 m above ground, b- sun higher than 60° and clear sky, e- sun 35°-60° and few broken clouds or clear sky, d- sun 15°-35°, cloudy.

The above described stability classification is known as Pasquill's stability classification which is the most popular one because of its simplicity.

3 Gaussian plume model

Gaussian plume model is used to calculate the concentration of a pollutant downwind of a point source. Figure 2 shows the three dimensional coordinates system and the Gaussian plume equation for the case when the value of z is zero, for calculating ground level concentration:

Where,

C (x,y) = concentration at ground level
Q = emission rate of pollutants, µg/s
H = effective stack height, m
U= average wind speed at effective stack height
σy &σz = horizontal & vertical dispersion coefficients, m, respectively

The dispersion coefficient depends on the atmospheric stability class and increase with the downwind distance from the source. Figure 3 gives values of the dispersion coefficients as a function of distance for various stability classes. The Gaussian plume equation can be used to predict ground level pollutant concentrations under different stability conditions for a given pollution source.

Figure 4 shows the downwind ground level concentrations due to emissions from a thermal power plant calculated for different stability classes. Note that the turbulence in an unstable atmosphere results in a high concentration near the stack. Downwind, however, concentrations drop off very quickly. The stable atmosphere, on the other hand, has a much lower peak. However, it continues to be appreciable for a considerable distance downwind.

As shown in Figure 5, the ground level concentration is also quite sensitive to stack height. In order to disperse pollutants over a larger area, stack heights in the range of 200 to 250 m are quite common. The stack heights shown in Figure 5 are effective stack heights, which are higher than the actual stack heights because of the buoyancy of the plume at the emission point, Figure 2.

It is possible to calculate average ground level concentrations over a specified period by integrating values occurring under different stability conditions and wind speed and direction. Such data can be presented in the form of isopleths as shown in Figure 6.

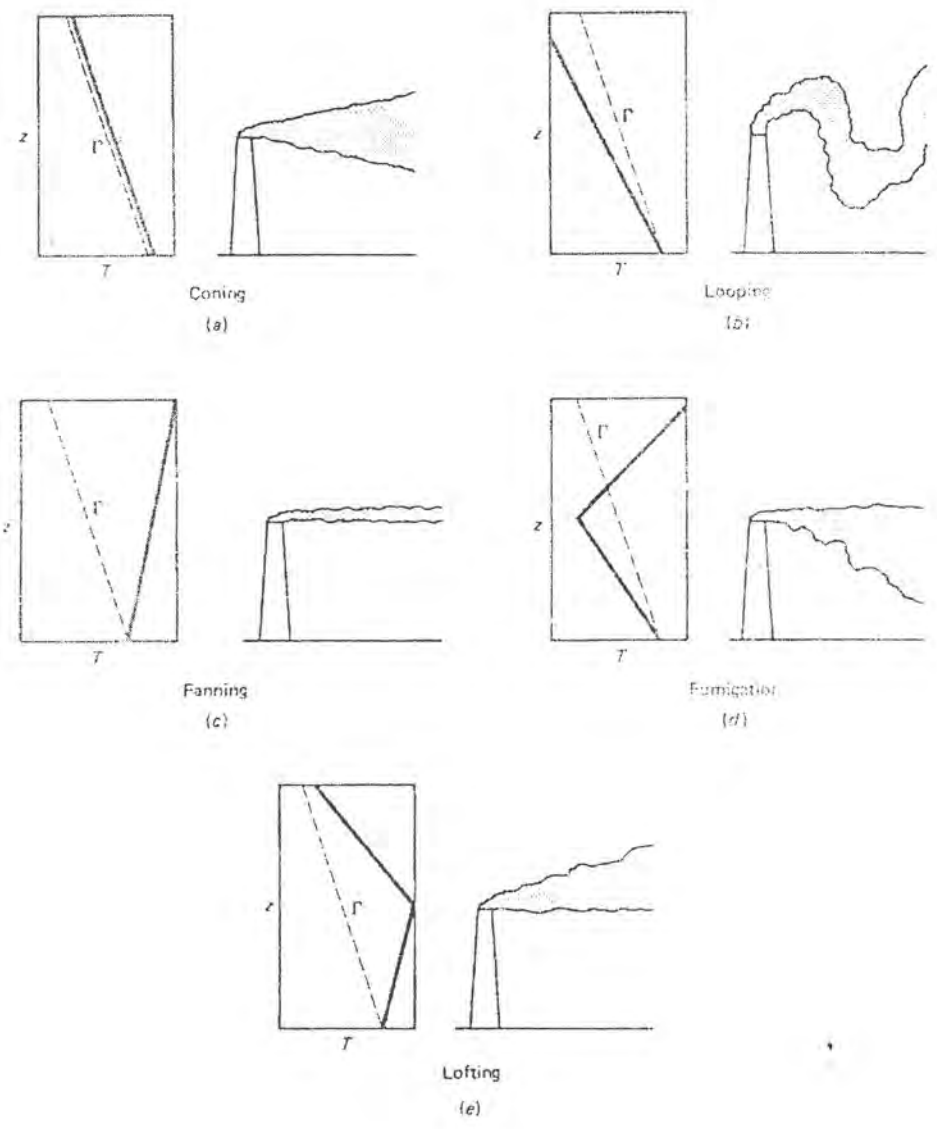
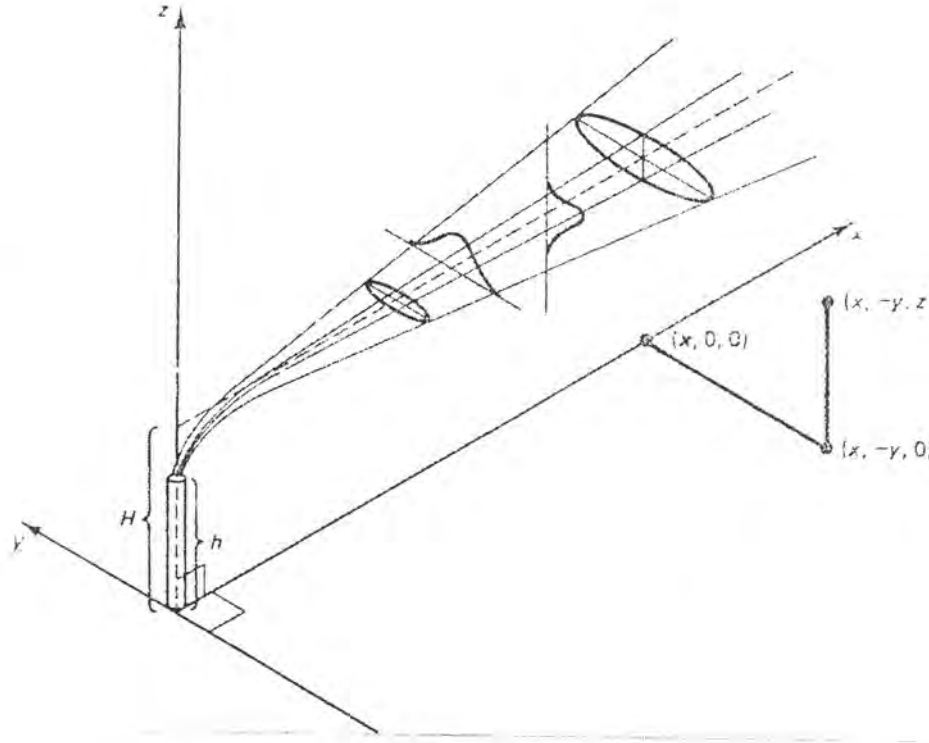


FIGURE 1 EFFECT OF LAPSE RATES AND STACK HEIGHTS ON PLUME BEHAVIOUR, (ADIABATIC PROFILE -------, ENVIRONMENTAL PROFILE ————).



$$C(x, y) = \frac{Q}{\pi u \sigma_y \sigma_z} \left(\exp \frac{-H^2}{2\sigma_z^2}\right)\left(\exp \frac{-y^2}{2\sigma_y^2}\right)$$

where $C(x, y)$ = concentration at ground-level at the point (x, y), $\mu g/m^3$
x = distance directly downwind, m
y = horizontal distance from the plume centerline, m
Q = emission rate of pollutants, $\mu g/s$
H = effective stack height, m, ($H = h + \Delta h$, where h = actual stack height, and Δh = plume rise)
u = average wind speed at the effective height of the stack, m/s
σ_y = horizontal dispersion coefficient (standard deviation), m
σ_z = vertical dispersion coefficient (standard deviation), m

FIGURE 2 PLUME DISPERSION COORDINATE SYSTEM AND THE GAUSSIAN EQUATION FOR GROUND LEVEL ($z = 0$) CONCENTRATION.

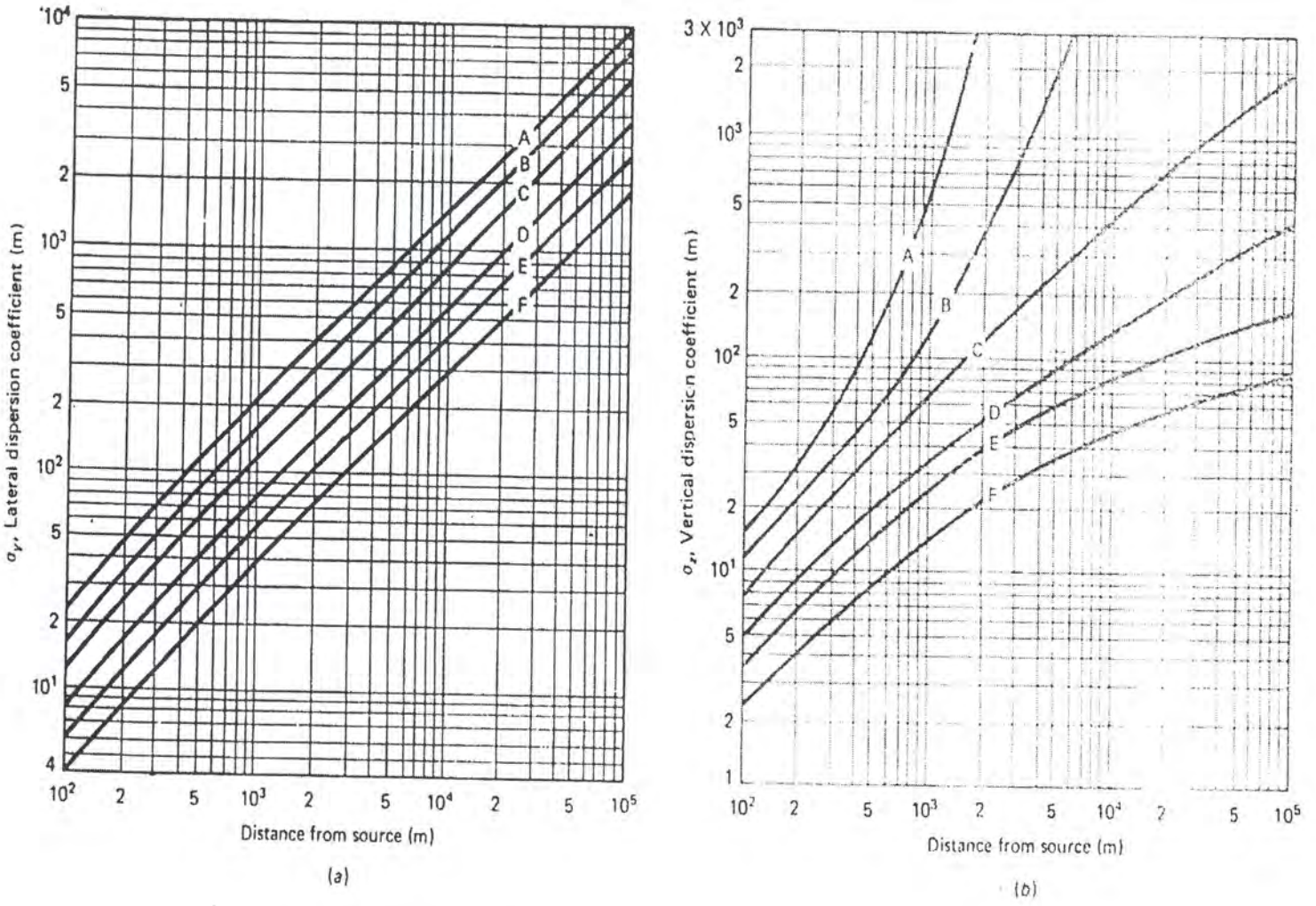


FIGURE 3 GAUSSIAN DISPERSION COEFFICIENTS AS A FUNCTION OF DOWNWIND DISTANCE.

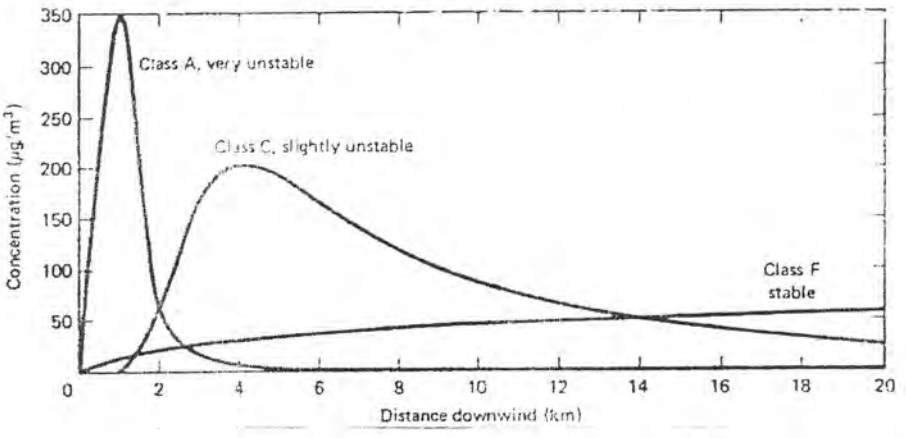


FIGURE 4 EFFECT OF STABILITY CLASSIFICATION ON GROUND LEVEL CONCENTRATION FOR A FIXED STACK HEIGHT.

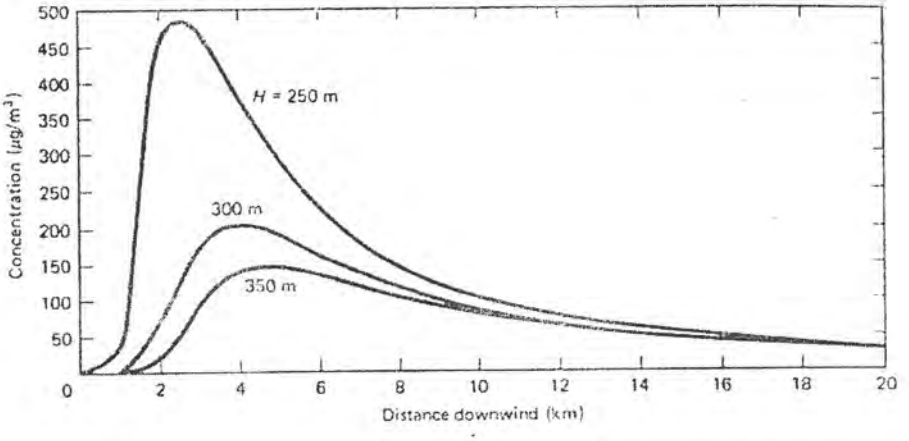


FIGURE 5 EFFECT OF STACK HEIGHT ON GROUND LEVEL CONCENTRATION FOR CONSTANT STABILITY CLASSIFICATION.

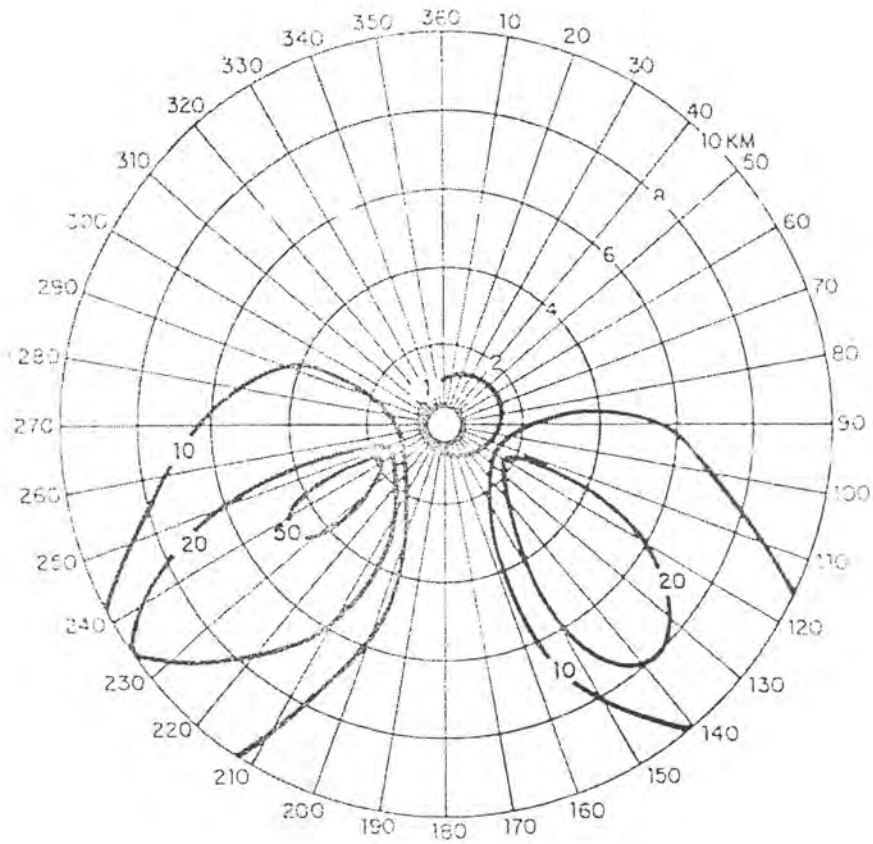


FIGURE 6 HYPOTHETICAL MONTHLY GROUND LEVEL ISOPLETHS OF POLLUTANT CONCENTRATION.

Chapter 5
Basic Chemistry Concepts

1 Elements, compounds and molecular weights

Table 1 lists some basic information regarding elements that an environmental chemist may encounter. Certain groupings of atoms act together as a unit in a large number of compounds. These are referred to as radicals and are given special names. The most common radicals are listed in table 2. The information regarding the valence and ionic charge given in the tables can be used to write formulas of compounds by balancing+ive and-ive charges. For example, sodium chloride will be written as NaCl, but sodium sulphate will be Na_2SO_4.

Most inorganic compounds when dissolved in water ionise into their constituent ionic species. Na_2SO_4 when dissolved in water will dissociate in two positively charged sodium ions and one negatively charged sulphate ion. Note that the number of +ive and-ive charges balance and the water remains electrically neutral.

The gram molecular weight of a compound is the summation of atomic weights in grams of all atoms in the chemical formula. This quantity of substance is also called a mole (mol). Some reagent grade compounds have a fixed number of water molecules as water of crystallisation associated with their molecules. This should also be accounted for in the calculation of the molecular weight.

Example 1

Write the molecular formula for aluminium sulphate (alum) given that the aluminium ion is Al^{3+}, the sulphate ion is SO_4^{2-} and that each molecule has 18 molecules of water of crystallisation. Calculate its molecular weight. What is the percentage of sulphur in the compound?

As the total number of +ive and -ive charges must be the same within a molecule, the lowest number of Al^{++} and SO_4^{2-} ions which can combine together is 2 and 3 respectively so that:

Number of +ive charges on $2Al^{3+}$ = 6
Number of -ive charger on 3 SO_4^{2-} = 6
Therefore the formula is $Al_2 (SO_4)_3 \, 18H_2O$

The molecular weight is
$2Al^{3+}$ = 2 x 27 = 57
3 SO_4^2 =3 x 96 =288
$18H_2O$ = 18 x 18 = 324
Total = 666

Percent sulphur = (3 x 32/666) x 100 =14.4

Name	Symbol	Atomic Weight	Common Valence	Equivalent Weight
Aluminium	Al	27.0	3+	9.0
Arsenic	As	74.9	3+	25.0
Barium	Ba	137.3	2+	68.7
Boron	B	10.8	3+	3.6
Bromine	Br	79.9	1-	79.9
Cadmium	Cd	112.4	2+	56.2
Calcium	Ca	40.1	2+	20.0
Carbon	C	12.0	4-	
Chlorine	Cl	35.5	1-	35.5
Chromium	Cr	52.0	3+	17.3
			6+	
Copper	Cu	63.5	2+	31.8
Fluroine	F	19.0	1-	19.0
Hydrogen	H	1.0	1+	1.0
Iodine	I	126.9	1-	126.9
Iron	Fe	55.8	2+	27.8
			3+	
Lead	Pb	207.2	2+	100.3
Magnesium	Mg	24.3	2+	12.2
Manganese	Mn	54.9	2+	27.5
			4+	
			7+	
Mercury	Hg	200.6	2+	100.3
Nickel	Ni	58.7	2+	29.4
Nitrogen	N	14.0	3-	
			5+	
Oxygen	O	16.0	2-	8.0
Phosphorus	P	31.0	5+	6.0
Potassium	K	39.1	1+	39.1
Selenium	Se	79.0	6+	13.1
Silicon	Si	28.1	4+	6.5
Sliver	Ag	107.9	1+	107.9
Sodium	Na	23.0	1+	23.0
Sulphur	S	32.1	2-	16.0
Zinc	Zn	65.4	2+	32.7

Table 2 Common radicals in water

Name	Formula	Molecular Weight	Electrical	Equivalent Weight
Ammonium	NH_4^+	18.0	1+	18.0
Hydroxyl	OH^-	17.0	1-	17.0
Bicarbonate	HCO_3^-	61.0	1-	61.0
Carbonate	CO_3^{2-}	60.0	2-	30.0
Orthophosphate	PO_4^{3-}	95.0	3-	31.7
Orthophosphate Mono-hydrogen	HPO_4^{2-}	96.0	2-	48.0
Orthophosphate di-hydrogen	$H_2PO_4^-$	97.0	1-	97.0
Bisulphate	HSO_4^-	97.0	1-	97.0
Sulphate	SO_4^{2-}	96.0	2-	48.0
Bisulphite	HSO_3^-	81.0	1-	81.0
Sulphite	SO_3^-	80.0	2-	40.0
Nitrite	NO_2^-	46.0	1-	46.0
Nitrate	NO_3^-	62.0	1-	62.0
Hypochlorite	OCl^-	51.5	1-	51.5

2 Equivalent weights and chemical reactions

Table 1 and Table 2 also give the valence and equivalent weight of the listed substance. Valance is determined as (1) the absolute value of iron charge, (2) the number of H^+ or OH^- a spacie can react with, or (3) the absolute value of change in charge on a specie when undergoing a chemical reaction. The equivalent weight is determined by dividing the atomic or molecular weight by the valence. A major use of the concept of equivalents is that one equivalent of an ion or molecule is chemically equivalent to one equivalent of a different ion or molecule.

Example 2

Express 120 mg/L Ca^{2+} concentration as $CaCO_3$

120 mag Ca^{2+}/L=120 mg C^{2+}/L x1 meq/20 mg C^{2+} x 50 mg $CaCO_3$/1meq

=300 mg $CaCO_3$/L

A balance chemical equation is a statement of combining rations that exist between reacting substances. Consider the reaction between NaOH and H_2SO_2.

$$2NaOH + H_2SO_4 = Na_2SO_2 + 2\ H_2O \quad (1)$$

It is seen that 2 mole (80g) of NaOH react with 1 mole (98g) of H_2SO_4. In terms of equivalents, the number of equivalents of NaOH (80 {molecular weight} divided by 40 {equivalent weight}=2 is the same as that of H_2SO_4 (98 {molecular weight} divided by 49 {equivalent weight}=2). Stated differently, in balanced chemical reaction the number of equivalents of combining reactants is the same. This concept is utillised in determination of unknown quantities in titrimetric analyses described in the following section.

3 Titrimentric methods of analysis

Titrimetric or volumetric method makes use of standard solutions, which are reagents of exactly known strength. It involves determining the exact volume of the standard required to react completely with the unknown substance contained in a known weight or volume of the sample. The standard of highest known purity and stable under conditions of storage is called a primary standard. If it is unstable, it is necessary to determine the purity of the standard periodically. Such a standard is called a secondary standard.

The strength of standard solutions is defined in terms of either normality (N) or molarity (M). A 1.0/N solution contains one equivalent weight of the substance in 1L of the solution. For a given reaction, if one is fixed the other is also known. A 0.05M H_2SO_4 will be 0.1 N (2 equivalents/ mole), since one mole of sulphuric acid combines with two moles of hydroxyl ion, Equation (1).

Example 3

Calculate the number of meq of H_2SO_4 present in 35 mL of 0.1 N standard solution.

The strength of 0.1 *N* solution = 0.1 eq/L = 0.1 meq/mL
Therefore number of meq present in 35 mL = 0.1 meq/ml x 35 mL = 3.5 meq.

One of the requirements of titrimetric analyses is that it should be possible to know the exact volume of the standard consumed by the unknown substance in the sample. This is achieved by using an indicator in the reaction mixture. The indicator causes a visual change in the appearance of the mixture as soon as the reaction is complete.

Example 4

Calculate the concentration of alkali present in a sample when 50 mL aliquot of the sample consumed 12.4 mL of O. 1 N standard H_2SO_4. Express your result in meq/L, *mg NaOH/L, mg $CaCO_3$/L.*

Standard acid consumed = 0.1 meq/mL x 12.4 mL = 1.24 meq
Therefore, the concentration of alkali in the sample
= 1.24 meq/50 ml x 1000 mL/1 L
= 24.8 meq/L
= 24.8 meq/Lx 40 *mg* NaOH/meq
= 992mg/L as NaOH
=24.8 meq/Lx 50 mg $CaCO_3$/meq
= 1240 mg/L as $CaCO_3$

4 Significant figures

If individuals in a group are asked to measure a line exactly 6 cm and 4 mm long using a scale marked in cm graduations only, they may report the result as 6.3, 6.2, 6.5, 6.4, 6.6 cm, etc. To avoid ambiguity in reporting results or in presenting directions for a procedure, it is the custom to use significant figures only. In a significant figure all digits are expected to be known definitely, except the last digit, which may be in doubt. Thus in the above example there are only two significant figures (the figure before the decimal point is certain, after the decimal point the figure is based on an estimation between to graduations of the scale). If more than a single doubtful digit is carried, the extra digit or digits are not significant.

Round off by dropping digits that are not significant. If digits greater than 5 are dropped increase the preceding digit by one unit; if the digit is less than 5, do not alter preceding digit. If the digit 5 is dropped, round off the preceding digit to the nearest even number: thus 2.25 becomes 2.2 and 2.35 becomes 2.4.

The digit 0 may at times introduce ambiguity. If an analyst calculates total residue of 1146 mg/L, but realises that 4 is somewhat doubtful and therefore 6 has no significance, he may round off the result and report it as 1150 mg/L. Obviously he can not drop the digit 0, although it has no significance. The recipient of the result will not know if the digit 0 is significant or not.

Zeros bounded by other digits only on the right side only are never significant. Thus, a mass of 21.5 mg has three significant figures. Reported in g, the value will be 0.0215, which will again have 3 significant digits.

In most other cases, there will be no doubt as to the sense in which the digit 0 is used. It is obvious that the zeros are significant in such numbers as 104 5.000 and 40.08.

A certain amount of care is needed in determining the number of significant figures to carry in the result of an arithmetic operation. When numbers are added or subtracted, the number that has fewest decimal places, not necessarily the fewest significant figures, puts

the limit on the number of places that justifiably may be carried in the sum or difference. The sum 0.0072 + 12.02 + 488 = 500.0272, must be rounded off to 500, because one of the numbers, 488, has no decimal places.

For multiplication or division, round off the result of the calculation to as few significant figures as are present in the factor with the fewest significant figures. For example, for the calculation (56xO.003462x43.22)/1.684, the result 4.975740998, may be rounded off to 5.0, because one of the components, 56, has only two significant figures.

Chapter 6
Basic Statistics Concepts

Every physical measurement is subject to a degree of uncertainty. A result that is not particularly accurate may be of great use if the limits of the errors affecting it can be set with a high degree of certainly. Statistical methods are used to evaluate the probable errors in analytical measurements and interpretation of environmental data. This module discusses some basic concepts of statistics, which a chemist should be conversant with in order to evaluate the accuracy of the laboratory data and the estimation of the environmental characteristics based on the results of limited samples.

1 Frequency distribution

Results of 44 replicate analyses for hardness of a sample of water are given in Table 1.

Table 1. Results of 44 replicate analyses for hardness, mg/l as $CaCO_3$

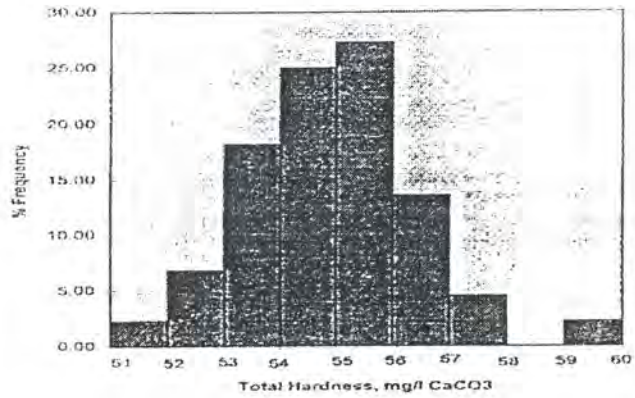
Class	Value	No. of Values in the Class	Frequency
(1)	(2)	(3)	(4)
51-52	51.2	1	0.0227
52-53	52.0,52.8,52.8	3	0.0682
53-54	53.1,53.1,53.3,53.4,54.4,54.5,54.5,54.6, 54.7,54.7,54.9	8	0.1818
54-55	55.1,55.1,55.3,55.3,55.4,55.4,55.6,55.7, 55.7,55.8,55.9,55.9	11	0.2500
55-56	56.2,56.3,56.7,56.8,56.9,56.9	12	0.2727
56-57	56.2,56.3,56.7,56.8,56.9,56.9	6	0.1364
57-58	57.3,57.5	2	0.0454
58-59	-	0	
59-60	59.1	1	0.2227

The date are classified in 9 classes, column (1) and arranged in each class according to their magnitude, column (2). By convention and observation equal to the upper value of the class is counted in the next higher class. For example the value 52.0 is not placed in class 51-52 but in 52-53. The number of values in each class are given in column (3). The ratio of number of values is a class to the total number of observation is called frequency and is given in column (4).

A plot of data of column (1) vs. column (4) is called frequency distribution diagram and is shown in Figure 1. For clarify of presentation, the frequency value is multiplied by 100 and shown as %.

Note that if the number of observation is increased and the class interval is reduced, the histogram can be replaced by a continuous curve.

Figure1: Example of a frequency distribution diagram



Central Tendency

Arithmetic mean: The arithmetic mean, $\overline{X}$, of a set of data is calculated by adding all the observed values of variable (results of analyses) and dividing it by the total number of observations:

$$\overline{X} = (X_1 + X_2 + \ldots\ldots\ldots X_n)/n \qquad (1)$$

where X_1, X_2, ... X_n are the observed values and n is the total number of observations.

The arithmetic mean is the most common measure of the central tendency. The mean value of the data of Table 1 was calculated as 54.9

Geometric mean: When there are a few very high values or very low, such as in the cases of bacteriological analysis, the arithmetic mean is not necessarily representative of the central tendency. In such cases the geometric mean, g, is used:

$$g = X_1 \times X_2 \times X_3 \ldots\ldots\ldots X_n)^{1/n} \qquad (2)$$

Median: The median is the middle value of the set of data. If the sample size n is an odd number, one-half of the values exceed the median and one-half are less. When n is even, it is average of the two middle terms. For the data of Table 1, it is 54.8, which is the average of 54.7 and 54.9, the 22nd and the 23rd terms, when the data are arranged in ascending order.

Mode: The mode is the most commonly occurring value. It is not widely employed as it forms a poor basis for any further arithmetic calculations.

Standard deviation

The data of Table 1 show that 52% of observations lie in the range of 54 - 56 and 84% in the range of 53-57. This tendency of observations to cluster (or not to cluster) around the mean value, 54.9, is measured by *standard deviation,* s. Standard deviation is calculated as:

$$s=\sqrt{\{X_1-\bar{X})^2\ (X_2-\bar{X})^2+.....(X_n-\bar{X})^2\}/(n-1)}$$

$$\text{or } s=\sqrt{\frac{\Sigma x_i^2-(\Sigma X_i)^2/N}{N}} \qquad (3)$$

A small value of s signifies that most of the observations are close to the mean value. A large value indicates that the observed values are spread over a larger range. For example, if the data of Table 1 has more observations in 52-53 and 57-58 classes and correspondingly lesser number in the central classes 54-55 and 55-56, the frequency distribution diagram will be flatter and spread wider at the base and the value of s will be larger.

The standard deviation has the same units as the quantity measured. The standard deviation for the data of Table 1 was calculated as 1.545 mg/L.

The square of the standard deviation is called the *variance*. If the random distribution of data is due to r different reasons, the total variance is the sum of individual variance.

Normal Distribution

Most frequency distributions for *random* observations, when the total number of observations is very large tending to be the same as the population, N, conform to normal distribution. The distribution is give by the theoretical equation:

$$y=\frac{e^{-(xi-\mu)2/\,2\sigma 2}}{\sigma\sqrt{2\mu}} \qquad (4)$$

where y = frequency of observations μ= the mean, and σ = standard deviation. Note the distinction made in the notations for number of observations, mean and standard deviation for a sample of a limited set of data used earlier.

The standard deviation is given by:

$$\sigma=\sqrt{\frac{\Sigma x_i^2-(\Sigma X_i)^2/N}{N}} \qquad (5)$$

For a normal distribution, 68.3 % of the total observations lie in the range $\mu \pm\sigma$, 95.5% in the range $\mu \pm 2\sigma$ and 99.7% in the range $\mu \pm 3\sigma$. This is illustrated in Figure 2.

The number of observations between any two limits of the variable can be equated to the area bounded by the frequency distribution curve, the ordinates at these limits and the x axis.

When the data set is small, more often than not, sample mean, $\bar{X}$ will differ somewhat from the population mean, μ. Any error in $\bar{X}$ causes a corresponding error in the standard deviation calculated with Equation 5. There is a tendency for the standard deviation value calculated to be small as the number of measurements becomes smaller. It can be shown that this bias can be largely eliminated by substituting the *degree of freedom* as (n-1) in the

calculation, Equation (3), which defines the standard deviation for a limited set of measurements.

The rationale for using (n-1) is as follows. When μ is not known, we must extract two quantities, namely, X and s from the set of data. The need to establish X from the data removes one degree of freedom: that is if their signs are retained, the sum of individual deviations must total zero; once (n-1) deviations have been established, the final deviation is necessarily known. Thus only (n-1) deviations provide independent measures for the standard deviation of the set.

2 Precision and Accuracy of Experimental Data

Classes of errors

The phenomena that are responsible for uncertainties in an analytical measurement can be divided in two broad categories: *determinate* or *system errors* and *indeterminate* or *random errors.* The total error is the sum of the two types of errors.

Determinate errors have assignable causes and are unidirectional. It may be possible to eliminate some of these, for example, errors because of improper calibration of the equipment, or presence of interfering substances in the sample. Errors inherent in the method, such as addition of a reagent in excess of theoretical requirement to cause an indicator to undergo colour change in a titration, may be difficult to eliminate.

Indeterminate errors are encountered whenever a measuring system is extended to its maximum sensitivity. The results fluctuate in a random manner about a mean value. The sources of these fluctuations can never be identified because they are made up of a myriad of instrumental, personal and method uncertainties that are individually so small that they can never be detected. For example, in he case of addition of an exact volume of reagent in an analysis through a pipette the uncertainties could be the time allowed for draining the pipette, the angle at which the pipette is held during delivery, temperature of the reagent, visual judgement of water level with respect to the graduation mark, etc. What is observed in the final result is then a summation of a very large number of minute unobservable uncertainties. The cumulative effect is likewise variable. Ordinarily they tend to cancel one other and thus exert a minimal effect. Occasionally, however, they act in concert to produce a relatively large positive or negative error.

Precision

The term precision is employed to describe the reproducibility of results. It can be defined as the agreement between the numerical values of two or more measurements that have been made in an identical fashion.

Absolute methods for expressing precision: The *absolute average deviation* from the mean is a common method for describing precision. The *spread* or *range* of a set of data is also a measure of precision and is simply the numerical difference of the highest and the lowest result. *Standard deviation,* described earlier, is a more significant measure of precision.

Example 1
From the data of replicate chloride analysis of a water sample given below, calculate the precision in terms of the average deviation from the mean:

Analysis	Chloride, mg/L	Abs. dev. from the Mean, mg/L
1	24.39	0.077
2	24.19	0.123
3	24.36	0.047
Total	72.94	0.247
	Mean = 24.313	ave. dev. = 0.247/3 = 0.082

Relative methods for expressing precision: It is frequently more informative to indicate the relative precision. The relative parameters are dimensionless and therefore can be used to compare two ore more sets of data. Thus, for example, the *relative deviation* of analysis 1, in the above example, is (0.077 X 100)/24.313 = 0.32%.

Relative standard deviation or coefficient of variation is defined as:

$$CV = \frac{100s}{x} \qquad (6)$$

Example 2
Monitoring results at three sampling locations are listed below. Compare the sampling records in terms of variability.

	A	B	C
	40.0	19.9	37.0
	29.2	24.1	33.4
	18.6	22.1	36.1
	29.3	19.8	40.2
x	129.28	21.48	36.68
s	8.74	2.05	2.80
CV	0.30	0.10	0.07

In terms of the coefficient of variation the concentration at A varies the most, followed by B and then C.

Accuracy

The term accuracy is used to describe the total error of the observation, which is the sum of the systematic and random errors. It denotes the nearness of the measurement to its accepted value.

In Example 1, if the accepted value for the chloride concentration is 24.35 mg/L, the absolute error of the mean is 24.31 - 24.35 = - 0.04 mg/L.

3. Propagation of errors

The indeterminate error or uncertainty is most commonly expresses as standard deviation. When the final result is computed from two or more data, each of which has an indeterminate error associated with it, the error of the result will depend on the arithmetic computations. The following examples illustrate the procedure to be followed:

Example 3:

For the sum

$$\begin{aligned} &+ 0.50\ (\pm 0.52)\\ &+ 4.10\ (\pm 0.03)\\ &- 1.97\ (\pm 0.05)\\ &\text{----------}\\ &+ 2.63\ (\pm\ ?\ ?) \end{aligned}$$

where the numbers in parantheses are the absolute standard deviations. Statistically the most probable standard deviation would be given by the square root of the sum of individual variances:

$$s = \sqrt{(\pm 0.02)^2 + (:\text{to}.03)^2 + (\pm 0.05)^2}$$

$$= \pm 0.06$$

Therefore the result could be reported as:

$$2.63\ (\pm 0.06)$$

Example 4:

The case when products and quotients are involved is illustrated in the following calculations:

$$\frac{4.10(\pm 0.02)\text{x } 0.0050(\pm 0.0001)}{1.97(\pm 0.04)} = 0.0104(\pm ?)$$

In this case it is necessary to calculate the relative standard deviations:

$$(S_a)_r = \pm \frac{0.02}{4.10} = \pm 0.0049$$

$$(S_b)_r = \pm \frac{0.0001}{0.005} = \pm 0.020$$

$$(S_c)_r = \pm \frac{0.04}{1.97} = \pm 0.020$$

$$(S_y)_r = \sqrt{(\pm 0.0049)^2 + (\pm 0.02)^2 + (\pm 0.02)^2} = \pm 0.029$$

The absolute standard deviation of the result will bel

$$S_y = 0.0104 \times (\pm 0.029) = \pm (0.0003)$$

Therefore the uncertainty of the result can be written as:

$$0.0104 (\pm 0.0003)$$

For calculations that involve both sums and differences as well as products and quotients, the uncertainties associated with the former are evaluated first and then the latter following procedures illustrated in the two examples.

Chapter 7
High-Volume Sampler

1 Introduction

The *high-volume (Hi-Vol) sampler* is the workhorse of air sampling and monitoring. The sampler uses a continuous duty blower to suck in an air stream. When fitted with a particle size classifier, it separates particles greater than 10 J.1m size from the air stream. The air stream is then passed through a filter paper to collect particles lesser than 10 J.1m size (PM_{10}). Gravimetric measurements yield values of suspended particulate matter (SPM), as the sum of the two fractions, and PM_{10}, the material retained on the filter paper.

The filter paper can be used to determine benzene-soluble organics, metals, such as Pb, Cd, etc., fluorides, radioactive materials and biologically active non- metals, sulphate, nitrate and ammonium.

The sampler can also be used to sample gaseous pollutants. A stream of unfiltered air is bubbled through a reagent, which either reacts chemically with the gas of interest or into which the gas is dissolved. Wet chemical techniques are then used to measure the concentration of the gas.

The following sections describe various components of the sampler, particularly with reference to 'Envirotech Respirable Dust Sampler (RDS), Model APM 460 NL'. The sampler design is based on the know how developed at National Environmental Engineering Research Institute (NEERI), Council of Scientific and Industrial Research (CSIR), Govt. of India. The sampler is widely used in India in the National Air Quality Monitoring Programme (NAMP) of the country.

2 Particle size classifier

SPM in air is usually very irregular in shape. While liquid particles present in mists and sprays tend to be spherical, the solid particles making up most dust and fumes fall into one of the three general classes: granular, flaky and needlelike.

For describing such agglomeration of particles, the concept of equivalent sizes is used. The equivalent size of a particle is determined on the basis of equivalent behaviour, such as settling velocity, of an ideal spherical particle.

Aerodynamic diameter is defined as the diameter of a spherical particle of density 1 g/cm3, having a settling velocity equal to that of the particle in question. As discussed earlier, the respirable or thoracic particles are found to have diameter less than 10 J.1m. This diameter for PM1o refers to the aerodynamic diameter.

The APM 460 NL Hi-vol sampler uses a cyclone type particle size classifier, illustrated in Figure 1, to separate out particles of diameter greater than 10 μm aerodynamic diameter. Ambient air laden with SPM enters the cyclone near

its top where the air stream is given a swirling motion. The resulting centrifugal acceleration moves the coarse and heavier air borne particles to the outer wall. These separated particles fall through the cyclone conical hopper and are collect in the sampling bottle placed at the bottom.

The air containing the reparable dust exits through a cylindrical outlet, mounted concentrically at the top of the cyclone, and enters the filter assembly.

3 Filter assembly

Figure 2 schematically shows the arrangement of the cyclone classifier, the filter assembly, and the blower in the Hi-Vol sampler. The filter assembly consists of two parts, a top cover connected to the outlet port of the cyclone and a filter adapter with a backing screen for the filter paper. A rectangular 20.3 cm x 25.4 cm (8 in x 10 in) glass fibre filter paper is placed on the backing screen and the top cover is bolted. Suitable gasket is used to obtain an airtight connection. The collected matter on the filter is classified as PM1Q.

NEERI has analysed the collected PM1o for a variety of dusts like coal, limestone, cement, fly-ash, etc., for their size. Table1. gives a summary of their findings.

Table 1: Maximum size range of particles collected as PM1o under different situations using APM 460 NL Hi-Vol sampler[a].

S.No.	Nature of dust	Specific gravity	Maximum size range,μm
1.	Coal	1.4-1.8	10-12
2.	Road side	2.0 - 2.2	8 -10
3.	Fly-ash	2.3 - 2.4	8-9
4.	Mining limestone/sandstone	2.5 - 2.7	7-9
5.	Cement	3.0 - 3.3	6-8
6.	Manganese ore	3.5-4.0	5-7

a- NEERI internal report

It is seen from the reported data that the particulate matter collected as PM1Q has a maximum size range of 7-12 μm, S.No. 1 to 4. For heavier particles of specific gravity 3.0 to 4.0, S. No.5 & 6, the maximum size range is 5 to 8 μm. This implies that for the latter case, the heavier particles in the size range of 1 0 μm were retained in the cyclone. Taking into account the heterogeneity of the characteristics of SPM, it is possible that the cut-off level is not exactly met in a practical field situation.

4 Air blower and flow measurement

A standard regenerative blower is used for sucking the ambient air through the High-Vol sampler. The blower is capable of maintaining a flow rate in the range of 0.9 to 1.4 m^3/min through the assembly.

Airflow is measured from the pressure drop across a calibrated orifice which is built in the lower part of the filter adapter. The manometer recording the pressure drop is graduated in terms of flow rate in m3/min.

A time totaliser is provided to record the period of sampling. It has been wired in such a way that it operates only when the blower receives power. Thus it records the true time in hours for which the sampler samples the air. Readings must be noted before and after each sampling occasion to determine the duration of the sampling. The total reading on the totaliser also facilitates timely preventive maintenance.

5 Gaseous sampling attachment

The Hi-Vol APM 460 NL can be used to sample gases with the help of APM 411
Gaseous sampling attachment. The sampling assembly is shown schematically in Figure 3. It consists of a set of 4 impingers (bubblers), carried in an ice tray. The impingers can be operated either in series or parallel according to the requirement. The impingers can be filled with upto 30 ml of the reacting reagent.

Gaseous sampling requires only 0.1 to 3 L/min of airflow through individual impingers. The impingers have a common outlet for the air after it passes through the reacting reagent. The outlet is connected to a tapping on the suction side of the blower for drawing in the air. The flow through the impingers is regulated by means of individual needle values, for each of the 4 impingers, and one common outlet. The airflow rate is adjusted/measured with a rotameter provided with the attachment.

Table 2 lists some of the air pollutants, which can be isolated using the attachment. Note that a supporting analysis method will be required for measuring the concentration of each pollutant.

Table 2: Gaseous pollutants and their absorbing solutions.

Pollutant	Absorbing solution
SO_2	Tetra chloromercurate
NO_2	Arsenite
O_3	Potassium iodide
HCl, HF, HBr	Sodium hydroxide
Cl_2	Methyl orange
NH_3	Sulphuric acid
H_2S	Cadmium hydroxide
CH_3SH	Mercuric acetate

6 Chemical Characterisation of PM_{10}

The particulate matter collected on the filter paper can be analysed using suitable extraction or elution procedures, such as acid digestion and

extraction with solvents. The extracts then can be analysed using suitable analytical methods such as ion chromatography, atomic absorption spectroscopy, gas chromatography, etc. for specific pollutants.

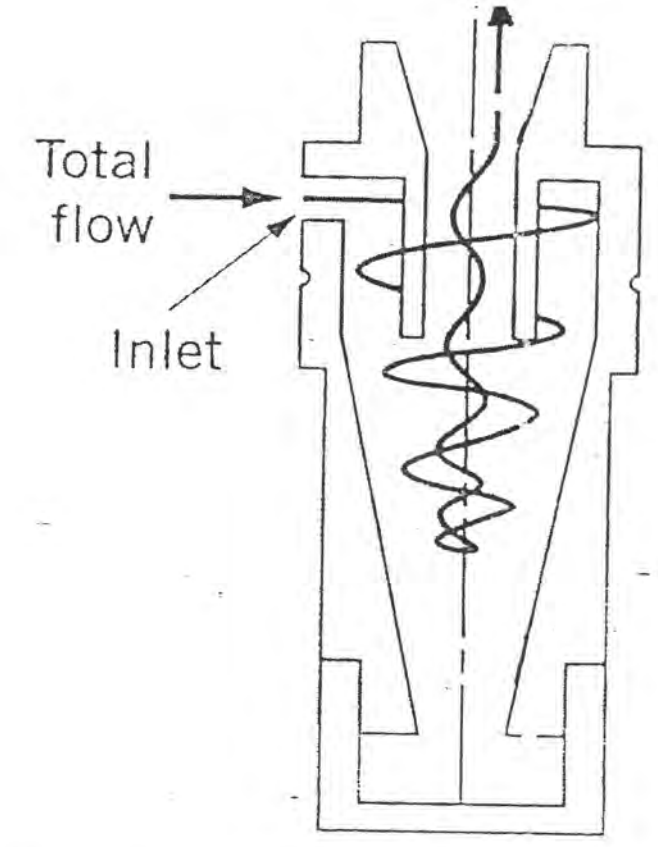


FIGURE 1 CYCLONE TYPE PARTICLE CLASSIFII

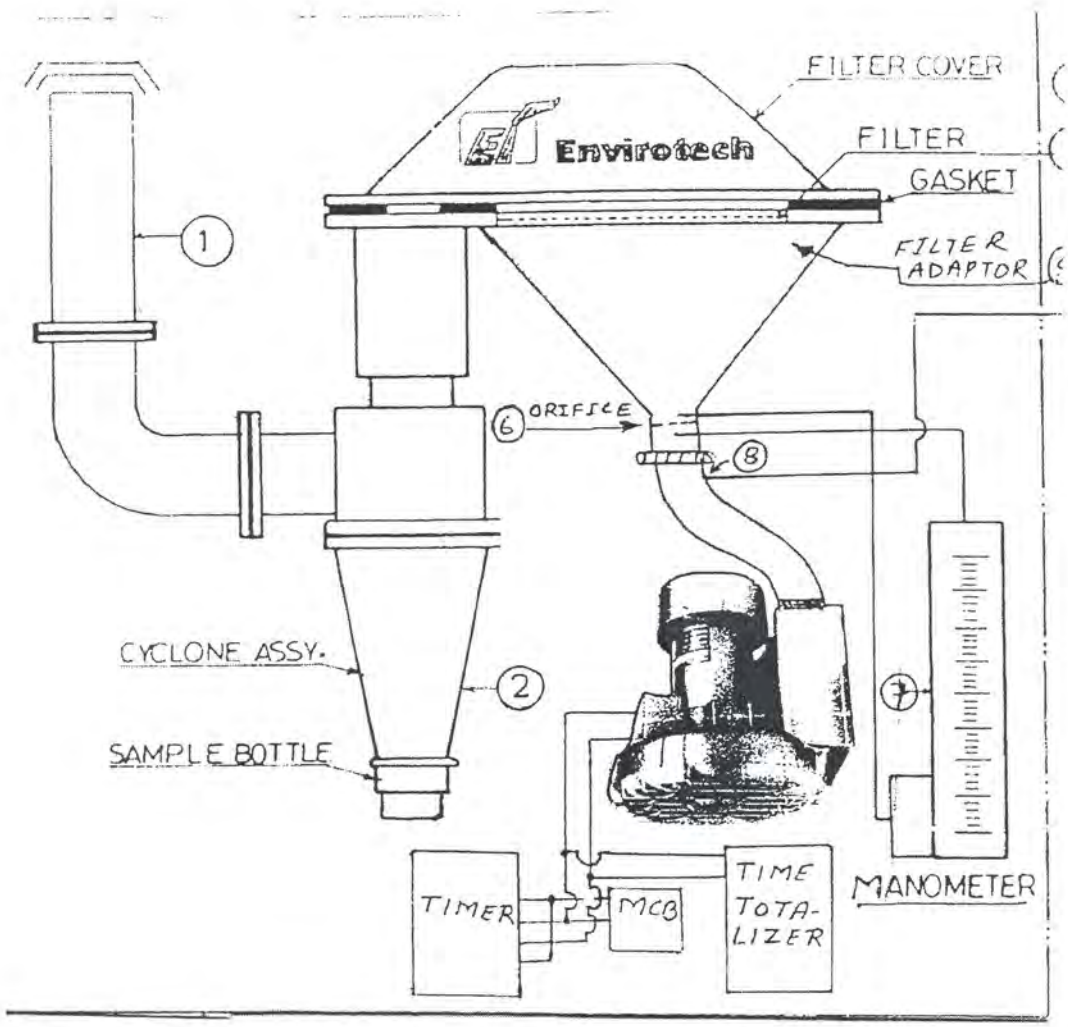


FIGURE 2 SCHEMATIC DIAGRAM OF HIGH VOLUME SAMPLER.

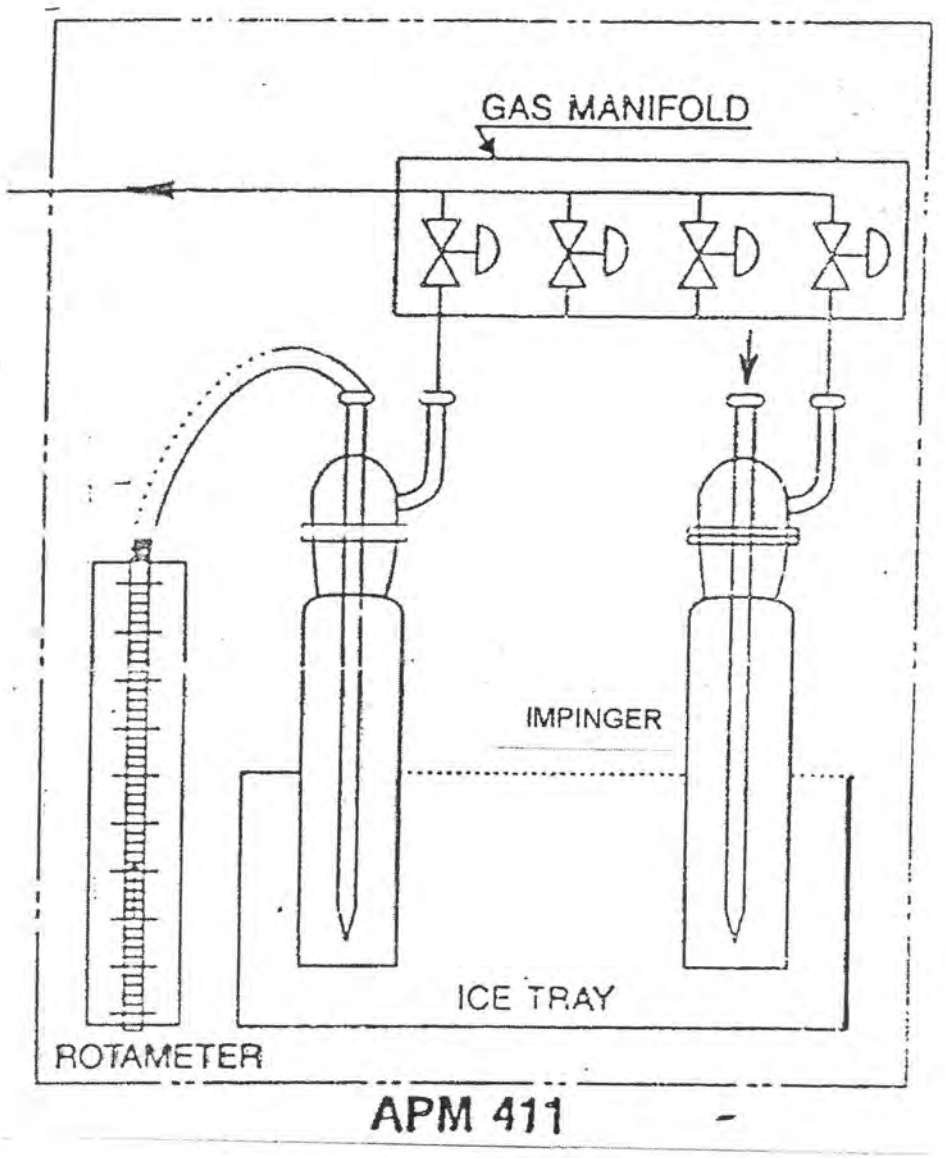


FIGURE 3 GASEOUS SAMPLING ATTACHMENT.

PRECAUTIONS TO BE FOLLOWED DURING ANALYSIS

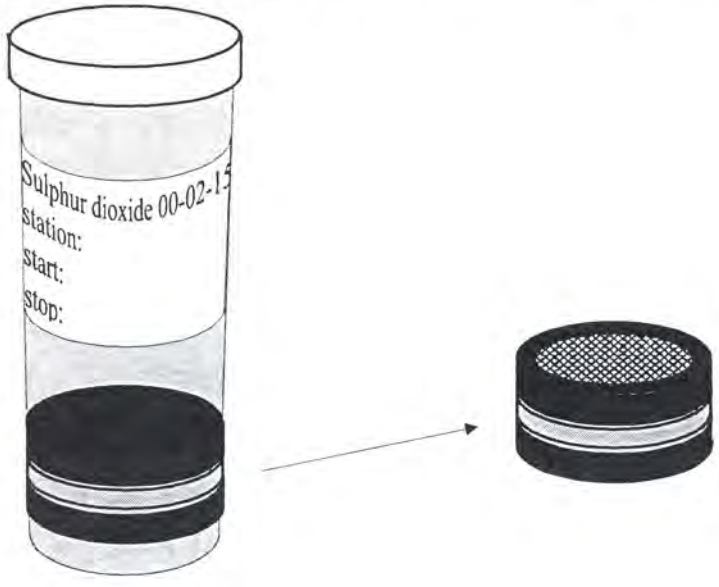
1. Glassware used in analysis need to be cleaned properly
2. Chemical whose strength changes with time need to prepared fresh (sodium metabisulphide)
3. Temperature of reagents used for analysis be brought at equal temperatures before mixing.
4. Chemical need to be stored as per recommendation (Ambered bottles, Away from heat and light)
5. Dry chemicals need to be transferred form bottles using glass rods only.
6. Reagent bottles need to be properly tightened.
7. Prepared chemicals need not to be left in the glasswares. These required to be transferred in the reagent bottles.
8. Always use Analytical Grade reagent for air pollution monitoring
9. Check quality of distilled water regularly.
10. Calibration and performance check of Balance and spectrophotometer need to done regularly.
11. Prepared reagent need to be stored after marking properly their name strength, date of preparation, expiry date and initial of chemist.
12. Replace/Regenerate desiccant of desiccators at regular intervals
13. Do not weigh chemicals using ordinary papers always use glaze papers for weighing.
14. Prepare fresh calibration graph once in 2 months.
15. Incorporate correction factor about assay of the reagent
16. Always desiccate dry chemicals as recommended in standard procedure.

Chaper 8

Sampling of sulphur dioxide and nitrogen dioxide using passive samplers

Background

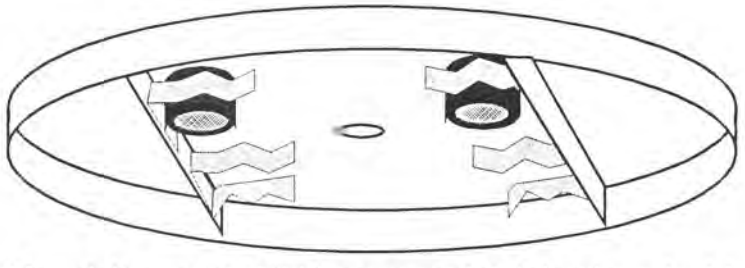
Passive (diffusive) samplers for measuring gaseous air pollutants are small, silent, accurate and easy to handle. They are now used world-wide to measure concentration of different gases. The samplers look like buttons and are stored in plastic containers, see the Figure below. The plastic containers are stored in a sealed plastic bag. The sampling starts as soon as the container is opened.



Sampler in a storage container

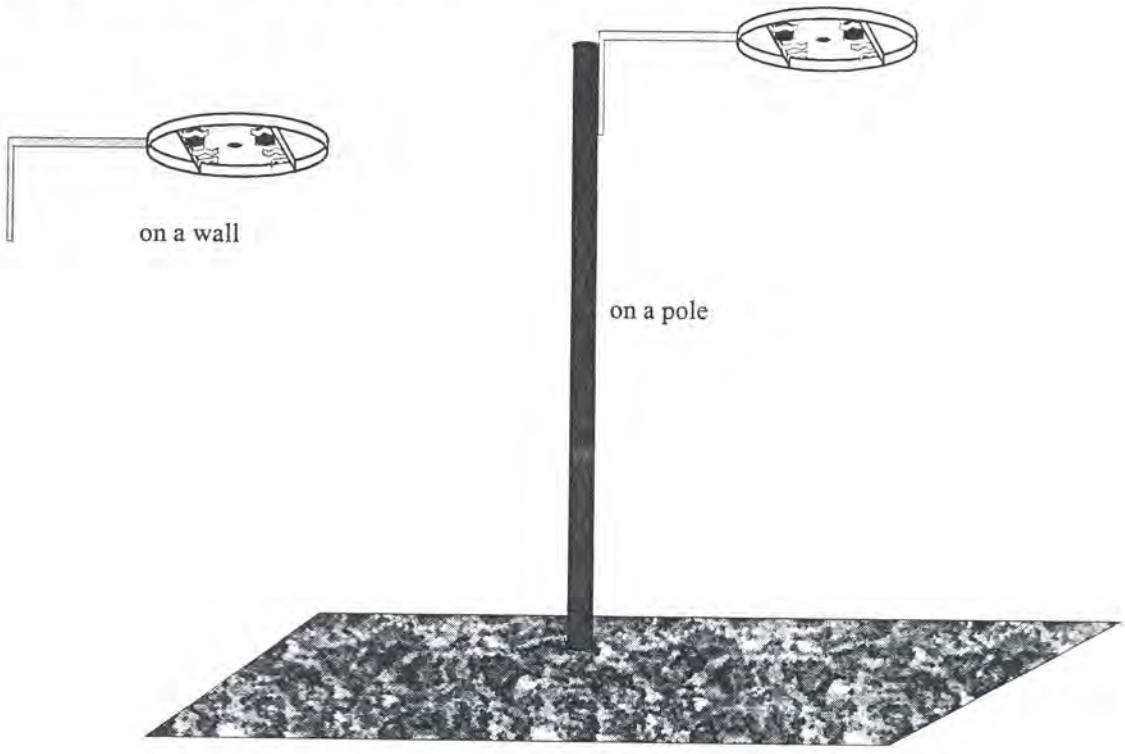
Sampling

The samplers should be mounted under a rain shield with the grey screen facing downwards. A special metal shield with clips to attach the samplers have been constructed, see below. First mount all samplers ,under the rain shield as shown below and always be shure the sampler is placed the right way (opening filter screen pointing downwards).



Mount the rain shield on a metal (aluminum) strip mounted horizontally out from a wall or a pole. It is important that the samplers are not too close to the ground or a wall. The distance should exceed 2 m above ground and 1 m

from a wall. The pole can be made of wood (50 x 50 mm) or metal and fastened in the ground in a proper way. This could be achieved by having a robust pole, bamboo stick or similar device placed in a hole so that the whole installation could be dismounted during change of samplers (by this there is no need for ladders *etc.* at the sampling location). For the mounting of samplers follow the instructions



Samplers mounted under a rain shield. The left one is mounted on a wall and the right on a pole in the ground.

The samplers have different colours for different pollutants. For sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) they look like this:

Sulphur dioxide Nitrogen dioxide

Exposure

Open the semi transparent storage container. The containers are marked with the name of the station.

- Dismount the sample pole to reach the rain shield
- Open the storage container and take sampler out of the container.
- Fix the sampler in the clip under the rain shield , screen facing towards ground.

- Write **starting date and time** on container label.
- Proceed with next sampler.....
- When the samplers are fixed, **fill in the protocol** (1 or 2 months sampling)
- Raise the pole and place it in the hole.

The screen of the sampler should face the ambient air. i.e. downwards.

After one or two months the samplers are removed and new ones are put up. The exposed samplers are put back into their storage containers. The container is closed and **the stop date (and time) should be written on the label** of the container. The average temperature could also be noted. **Don't forget to put the storage containers back in the plastic bag and seal it** before returning them to the laboratory (every second month is enough).

The address to the laboratory is:

If it is mailed as a letter:
IVL
Laboratoriet
P.O. Box 47086
SE-402 58 Gothenburg
Sweden

Or as a parcel:
IVL
Laboratoriet
Dagjämningsgatan 1
SE-415 09 Gothenburg
Sweden

If you have any questions don't hesitate to contact me.

tel: +46 31 7256 245
telefax: +46 31 7256 290
E-mail: Karin.Sjoberg@ivl.se

Chapter 9
Deposition monitoring – Sampling with bulk collector

This manual concerns daily collection and handling of deposition samples with the ordinary Swedish summer equipment. Precipitation sampling in the open field.

1. Equipment

At each site one sampler for bulk precipitation is located. Precipitation samplers (standards for Swedish deposition monitoring) are placed in a open field area. Vaoid windy places as much as possible.

1.1.Equipment

- Summer equipment is used when precipitation mainly consists of rain.
- The equipment consists of a funnel A (diameter 20.3 cm). Within this large funnel a smaller funnel (B), contains a screen, is placed to protect the sample from litter and evaporation. The sample is collected in a 5 L bottle (D). The sampling equipment is placed on a pole (F) equipped with a plate (E), approximately 1.5 m above the ground. (Figure 1)

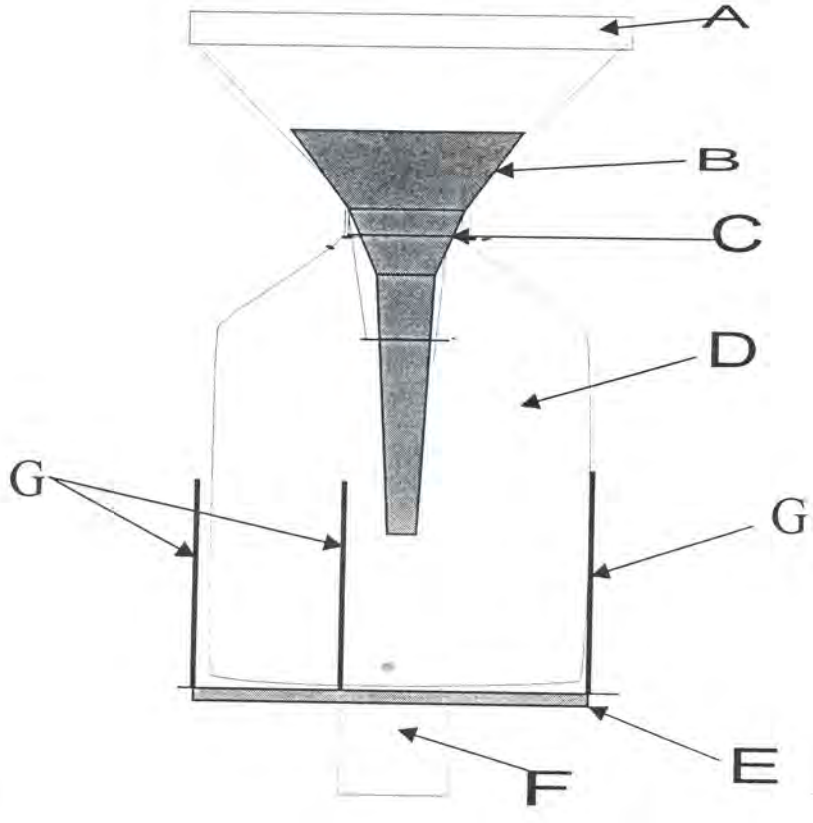


Figure 1: Open field collector for percipitation. **A:** *Funnel of polyetene ca 200 mm dia.* **B:** *Inner funnel of polyetene with small opening.* **C:** *Cap, leakage free connection.* **D:** *Polyetene bottle (5L).* **E:** *Bottom plate fastened onto the pole.* **F:** *Pole of wood (50x50 mm) length ca 110 cm above ground.* **G:** *Four rods to keep the equipment in place.*

- The bottle can be equipped with plastic bags of polyethylene inside in order to minimise the need of washing and rinsing of the bottles.

2. Sampling procedure

The following equipment for sampling at one sitea (open field) is needed:
- Replacement plastic bags for 5 L bottles
- Sample containers (1 or 2 L polyetene bottle)
- One 5 L bottle with wide opening
- Field protocol, pencils
- 2 L measuring cylinder
- Spray bottle for DD-sampling
- Deionized water for rinsing

2.2 Open-field

Sampling of bulk precipitation on an **open field** (Swedish monitoring standard equipment)

- Unscrew the cap (**C**) of the sample collector.
- Pour the sample into the sample container. Fill the sample container.
- Measure the rest of the volume using the 2 L measuring cylinder, note on the field protocol (be sure to include the surplus water from the filling procedure)
- If necessary rinse the collecting bottle, put a new plastic bag (larger size) into the 5 L bottle and close the cap.
- Check the collecting funnel and empty possible insects *etc.*, if necessary rinse with deionized water, also the small inner funnel. Put the funnel back and make sure it is horizontally positioned and properly fixed.

3. General instructions

- Make sure to note following information on the field protocol; date, volume, reasons for discarded samples and possible other factors that might influence the results, for example bird droppings and insects.
- Make sure that sample number, location and sample date (proper identification of samples) is noted on the sample container before analyses.
- Keep vegetation away from the collectors in the open field.

- Equipment should be kept in a neat and proper way. Avoid, as far as possible, touching parts, which will be in contact with water, samples (use plastic gloves or folded plastic bags). Rinse with deionized water when required.
- Be aware of contamination risks when handling equipment, sampling, etc in order to avoid contamination!

4. Washing

- Soon after sampling - used equipment shall be washed/rinsed.
- Since the 5 L containers always are used for the same sample location (preferably), it is enough to wash/rinse with deionized water. Let dry upside down. Store with cap on.

In a time restricted project, this should be done following termination of the measurement phase, and sampling equipment stored properly for future use.

CHAPTER 10
Instructions for using the MISU wet only collector

The following gives some hints on mounting, operating and trouble shooting for the wet only collector based on previous experiences. A suggestion on how to exchange sample bottles is also included. Since the site conditions vary, some alternatives are given.

Mounting of wet only collector

The following give examples of ways to mount the collector that have shown to be suitable. If mounted on the ground the easiest is usually to use a wooden pole (figure 1 and 2).
On rock, drill three holes and use pins to fasten the pole and props. On a platform (flat roof or similar) where holes can not be drilled, make a wooden frame with (very) heavy weights on it or use one big or tree smaller slabs of concrete to fasten the pole and props. The last mode should of course be dimensioned with regard to strongest winds on the location. The pole is fastened to the collector between the cylindrical part and the motor box (figure 2).

The height of the opening of the funnel can be about 1.7 m above ground. It is important with a step on the ground so that the operator can look down into the funnel and wash it without problem.

Preferably position the collector so that the lid swings away from the most frequent (or strongest) wind. Adjust the collector to be approximately vertical.

Sensor should be tilted somewhat (to let rain water run off) and facing the most frequent or strongest wind (during rain). The angel of the sensor against horizontal can be adjusted slightly by loosening the nut at the sensor (too much turning will damage the four electrical leads inside).

The collector is quite rugged and has shown to withstand high winds. The lid may however come loose and blow away. It is thus important to fasten the lid itself very tight to the holder.

The solar cell panel should be located well away from the collector (~ 3 m) and lower (0.3 to 1 m above ground) to avoid splash of rain from the solar panel entering the collector. Mounting can be done in the same way as the wet only collector, with one pole and two props (cf. Figure 4) or with four individual legs. Orient the panel in such away that can receive maximum flux of light, which is usually towards the south and slightly tilted from vertical to let water run off. The control box can preferably be mounted on the pole below the panel. Note that the panel can catch a great deal of wind. Be careful to dimension the support with regard to strongest winds on the site.
Put the sealed battery in the control box.

Mode of operation:

The battery (12 V) is to provide current during night and take up over voltage from the solar cell panel. The battery is of the sealed type. Using an ordinary car battery must be avoided due to the risk of contamination of samples from the sulfuric acid in the electrolyte (0.02 µl will give a noticeable effect). Connect the wo collector to battery and solar cell panel as shown in principle in figure 1 and 5. Let the cable rest on the ground and secure it there to avoid that men or animals stumble on it. Do not connect the solar cell panel directly to the wo collector without battery (the higher voltage during sunshine may damage the electronics in the wo collector). When electrical power is applied he first time the lid will open and then close after some time.

The lid makes a very tight seal against the "collar" around the funnel provided that the rim of the lid is undamaged. The position of the lid on the collar can be adjusted by moving the motor box slightly up or down relative to the cylindrical part.

A droplet (even a very small one) makes an electrical contact between the gold plated electrodes on the sensor. The red and the yellow lamp light up, the red signalling contact on the sensor and the lid starts to open. When water is drained of/evaporated the red light goes off but the yellow light is still on and the lid remains open. Some two minutes after the red light has gone off the yellow light also goes off and the lid starts to close. This delayed function is to prevent the lid from repeatedly open and close during very light rain.

The heating of the sensor makes it (intentionally) insensitive to dew. The sensor should feel warmer than other similar objects. For testing the sensor (and open the lid) it is enough to wet a finger briefly and touch the sensor.

A control for the solar cell panel measures the charge of the battery. If voltage is below 10 V the load (the wo collector) is disconnected to protect the battery against further depletion. When voltage is above 10 V the load is connected again. The wo collector is intended for 12 V DC but can operate down to about 9 V.

There is a fuse in the wo collector (thermal type). Operation can be resumed by disconnecting power, waiting and then connect to the battery again.

The collection bottle can be either 5 l or 2 l (with capacity of about 160 and 65 mm of rain respectively) (figure 3). The collection bottle is put in from below and fastened by screwing.

Maintenance:

The funnel and lid shall be cleaned regularly according to project recommendations (see also below).

The sensor needs to be cleaned occasionally (how often depends on local conditions). Use a piece of tissue paper or clean cloth to wipe of the sensor. Do not use abrasive material or metal parts as this will damage the sensor and shorten its lifetime.

At low latitudes the plastic material is likely to deteriorate after a few years. The lid and collar should be replaced when they become brittle and before they crack. (The advantages of using this plastic material far outweigh the drawback of limited lifetime).

Procedure for sample collection (suggestion)

This has (according to circumstances) been written without prior knowledge of instructions that will be given by the network committee. Regard it as a suggestion among others based on experience. It is assumed that collection bottles with content can not be transferred to the analysing lab (which, in principle, would be the best mode of operation), but instead that the a small part of collected rainwater is transferred to a transport bottle and the collection bottle is used again after cleaning.
Sampling procedure is given for normal collection. A QC routine is also included which includes collection of wash water from 1) the funnel after a few dry days with lid closed 2) washing of a cleaned funnel and 3) the wash water from the spray bottle used. This will reveal tightness of the lid and the how well the operator can clean the funnel. It can be repeated once to twice a month, more often in the beginning.

The following should be available at the station:
Supply of DI water (deionized water - with conductivity less than about 2 µS/cm).
Collection bottle(s) (cleaned)
Transport bottles (100 ml? - with thymol added beforehand at a lab if preservative is to be used)
Transport bottles with samples (if possible in refrigerator)
Small plastic tray
Balance (preferably electronic with sensitivity of 2 or 5g)
Log for rainwater collection

To bring along when collecting sample from the wo collector:
Equipment and bottles can conveniently be carried to the collector in a bowl or small plastic box. This provides a place to put the parts and bottles and avoid contamination of them. There should be room for two, preferably three, collection bottles (5-l).

Take along one cleaned collection bottle, a spray bottle full with DI (deionized) water, brush in plastic bag, pipe cleaners in plastic bag, disposable plastic gloves in plastic bag, notebook and pencil. If required also cotton gloves (to make it easier to take on the plastic gloves),

Wash hands and avoid dusty clothing.

Check every day at a given time (e.g. 8:00, am) if rain has fallen since previous visit.
If sufficient rain has fallen (usually >0.5 mm or >15 ml) the sample is to be collected.

- Take along the box with content as above to the wo collector
- Read off and write down open time and number of openings
- Open lid (put finger on sensor)

- Remove power cable from wo collector with lid open- to avoid that lid closes during the procedure
- Remove the collection bottle with rain sample. Put the bottle in the box and move the cap from the "new" bottle.
- Remove any debris from funnel (use gloves). Use brush for cleaning if appropriate and pipe cleaner in the narrow spout
- Wash with DI water from spray bottle, let drain, tap gentle on collector to remove most of remaining droplets
- Put in the new bottle and screw it on gently (should not be tight- to allow air to pass trough the threads during rain)
- Connect cable
- Check later that lid has closed

If there is only a small amount of rainwater (< 15 ml), estimate amount by eye and empty the bottle. Put bottle back. If so required after washing of the bottle or by using the new, cleaned one.

Follow up after collection

- Use a clean table. Clean the table, wash hands and avoid dusty clothing.
- Weigh bottle(s), one by one and record weight (bottle with cap + water). Also record bottle weight (with cap, marked on bottle).
- Mark transport bottle (e.g. with date, station code and "wo". In case of a wash test, mark with date, station code plus "wϕ", "w1" and "w2" respectively (see below in chapter quality control).
  If thymol is to be used as preservative it can be added beforehand (at the responsible lab) in the transport bottles (40 mg for 100 ml of sample).
- Remove the cap, which should be placed on table or on a clean paper with opening down. Place transport bottle in the small tray and the collection bottle outside on the table. Fill the transport bottle up to the rim by pouring directly from the 5-l collection bottle. Do not use any funnel. Do not worry about water spill as long as there is enough water to fill the bottle.
- Clean collection bottle. (gloves on). Shake vigorously (cap on) with remaining rainwater and pour out. If the bottle is still dirty, add more DI water and use brush. Pour out. Wash with three portions of DI water (30-50 ml). Put on cap and store till next time.
- Fill in the log. Note anything that may have affected sampling such as very strong winds, dust stirred up from ground with wind, time of generator in operation (if used) and any damage or malfunction of the instruments. Record also meteorological conditions if not recorded automatically.

Quality control (suggestion)

QC - to be performed according to schedule and after minimum of, for instance, 3 days with no rain

- Bring box with two cleaned 5-l collection bottles (if available) with caps, one transport bottle (100 ml?) marked with date and "wϕ", spray bottle with DI water, brush, gloves, notice book and pencil
- Record elapsed time and number of openings
- Open lid (put finger on sensor)
- Remove power cable (when lid is open)
- Put on gloves
- Spray about 60 ml of DI water over the whole funnel and let drain into the existing collection bottle.
- Remove the bottle and mark it temporarily with "w1" e.g. on a piece of tape
- Clean funnel thoroughly with brush and water from spray bottle, clean also the collar and lid inside and outside. Use pipe cleaner for the narrow spout in the bottom. Do not collect any of this water
- Spray lid, collar and all of inside of funnel carefully and let water drain (do not collect this water).
- Put in a new clean collection bottle, temporarily marked with "w2", below the funnel
- Spray the entire funnel with about 60 ml of DI water.
- Remove the bottle and put it in the box. Put on the cap from the remaining bottle
- Unscrew the cap of a transport bottle and spray about 60 ml DI water into it. Put on the cap again. (this is w0)
- Put a new 5-l collection bottle in the wo collector
- Connect cable
- Check later that lid has closed

Explanation: w0 is a control of water purity, w2 is a measure on how well operator can clean funnel and in particular how he can avoid contamination during that operation. w1 is a measure of lid seal. When some statistics have been accumulated comparisons can be made between wϕ, w1, w2 and rainwater concentration. Very instructive when results from the chemical analyses arrive!

Trouble shooting:

If the red light does not go off when all wetness on the sensor is away it is usually due to remaining material on the sensor. Clean more carefully with a piece of wet clothing. If this does not help remove the sensor by unscrewing the nut at the motor box and pulling shaft outward. If the red light goes off, there must still be a contact on the sensor. Connect the sensor again to the collector and inspect the sensor carefully for any bridge between electrodes. Try a non-metal brush (i. e. a toothbrush) or a wooden stick to see if it can be removed.

If the red light goes off but the yellow light is still on for many minutes, the error is usually not easy to cure. Try to disconnect and then reconnect power. If the error remains it requires special consideration. It can either be due to a fault in the electronics or a malfunctioning of the switches on the motor axis.

If lamps do not light up, as they should, check first the voltage of the battery and power supply. Remember that load is disconnected if voltage is below 10 V. If the voltage is to low try to find if the reason. Check connections for abnormal drain of the battery (i.e. a short-circuit). Second, disconnect and after some time connect power to the wo collector (the fuse may have been activated). If the battery has been exhausted, it may not take charge again. It has then to be replaced. If the error persists it can either be found in the circuit board or in the switches. This requires special consideration.

If the collector is properly maintained the likelihood of a malfunctioning is small. The solar cell panel has also shown to be very dependable. Should a more difficult error arise it is recommended that one of the above persons be contacted before further action. If there is some error on the circuit board the best way is to replace it with a
new one and send the faulty for repair.

Site selection

The location of the collector is important in order to obtain representative samples. It is here assumed that a site is selected that meets the required representativeness.
The final mounting of the collector should minimise the very local influence on the collector. Such factors are, among others: dust stirred up from the ground (or from a platform), animals grazing in the vicinity, splash from the ground or from structures above/around as well as positions exposed to strong winds or particularly strong local turbulence (that reduces the sampling efficiency). The collector should be easily accessed and comfortable to work with.

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Figure 1 Wet only collector and solar panel

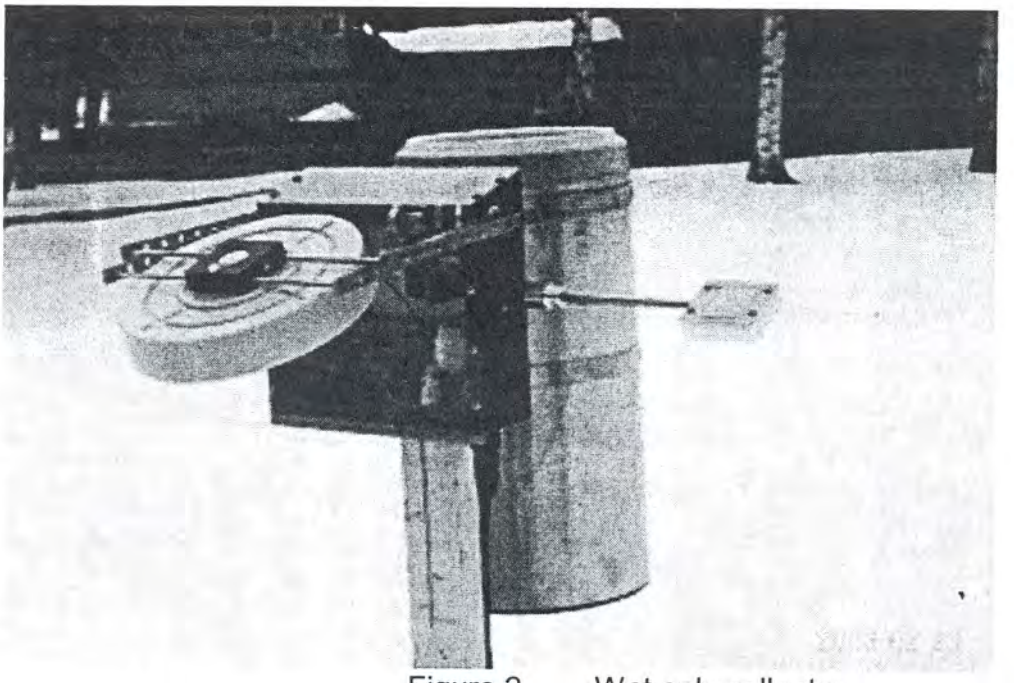


Figure 2 Wet only collector

Figure 3: Funnel and collector

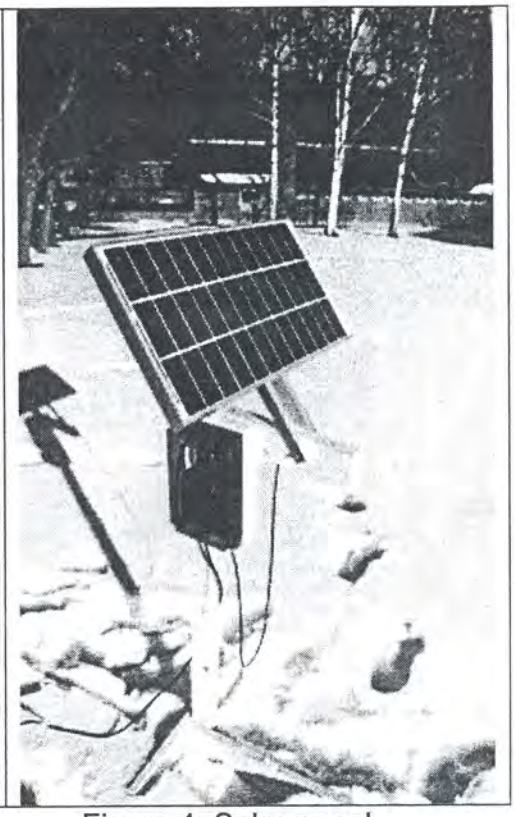


Figure 4: Solar panel

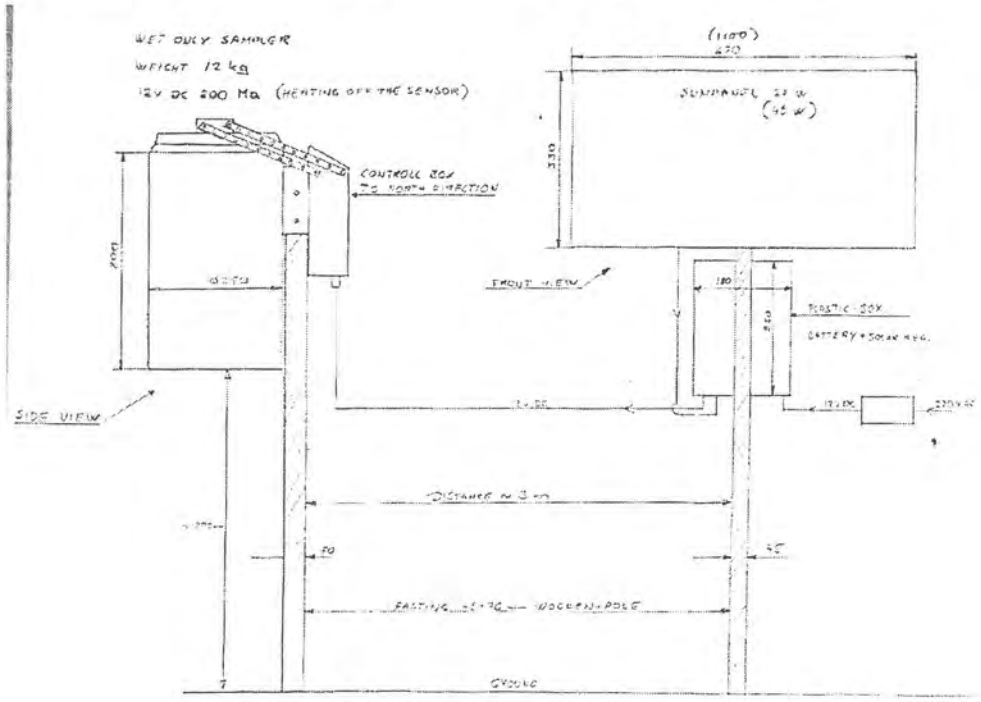


Figure 5 Drawing of the equipment (wet only collector and solar panel) distances in mm unless stated

Chapter 11
Spectrophotometer meter

1. Introduction

Absorption Spectroscopic methods of analysis rank among the most widespread and powerful tools for quantitative analysis. The use of a spectrophotometer to determine the extent of absorption of various wavelengths of *visible* light by a given solution is commonly known as *colorimetry*. This method is used to determine concentrations of various chemicals which can give colours either directly or after addition of some other chemicals.

As an example, in the analysis of phosphate, a reaction with orthophosphate is made, to form the highly coloured molybdenum blue compound. The light absorption of this compound can then be measured in a spectrophotometer.

Some compounds absorb light in other than the visible range of the spectrum. For example, nitrates absorb radiation of 220 nm wave length in the UV region.

2. Theory

Absorption Spectroscopic methods of analysis are based upon the fact that compounds ABSORB light radiation of a specific wavelength. In the analysis, the amount of light radiation absorbed by a sample is measured. The light absorption is directly related to the concentration of the coloured compound in the sample.

The wavelength (λ) of Maximum Absorption is known for different compounds. For example, the coloured compound formed for analysis of Phosphate (molybdenum blue) has maximum light absorption at λ= 640 nm. Conversely, a minimum amount of light is *transmitted* through the compound at λ= 640 nm. This is shown schematically in Figure .1

Figure 1: Light Absorption and Transmission by Phosphate-molybdenum blue compound. Schematic diagram showing maximum light absorption (and minimum light transmission) at λ= 640 nm.

The Beer-Lambert Law

The Beer-Lambert Law is illustrated in Figure 2. The Absorbance (or optical density) and Transmission (or Transmittance) of light through a sample can be calculated by measuring light intensity entering and exiting the sample,

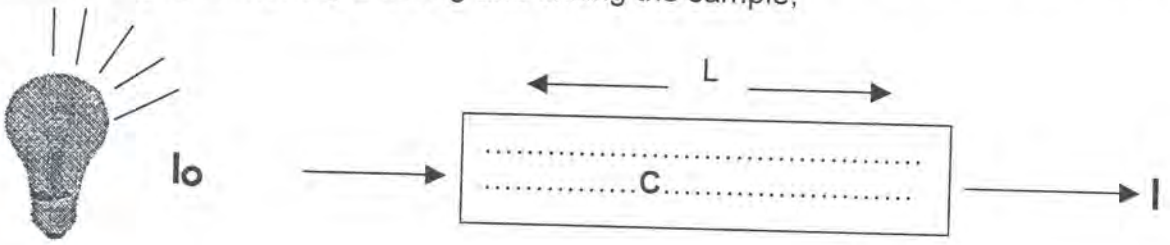


Figure 2: Light energy of Intensity '1_0' passes through a sample with concentration 'C'. Some light energy is absorbed by the sample. The amount of light energy exiting the sample has Intensity 'I'

The following terms are defined:

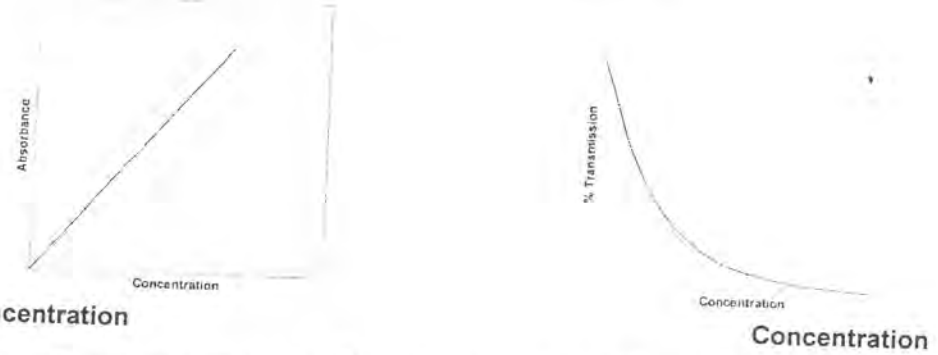
- Light Intensity entering a sample is "10"
- Light Intensity exiting a sample is "I"
- The Concentration of analyte in sample is "C"
- The length of the light path in glass sample cuvette is "L" .
- "K" is a constant for a particular solution and wave length

The Beer-Lambert Law is given by the following equations:

$$\text{Light Absorbance (A)} = \log\left(\frac{I_o}{I}\right) = KCL$$

$$\text{Light Transmission (T)} = \frac{I}{I_o} = 10^{-KCL}$$

Plots of absorbance and transmission versus concentration of the analyte in sample according to the above equations is shown in Figure 3,



Concentration

Concentration

Figure 3: Beer-Lambert Law relates the amount of light Absorbance (A) by a solution to the Concentration (C) of a compound in solution and the length of light path:

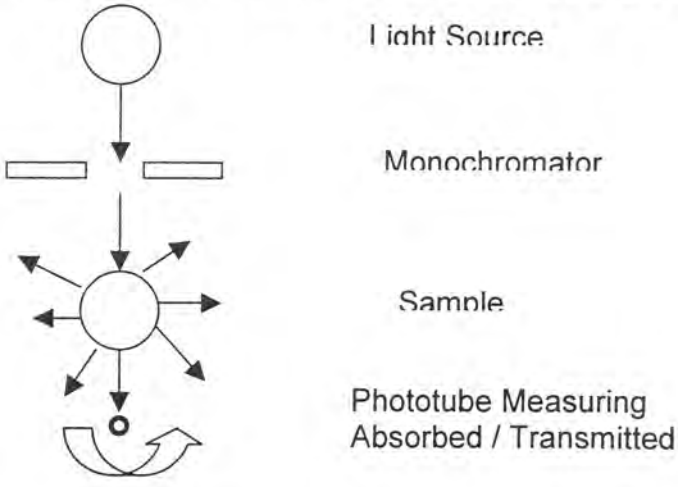
- **As Concentration (C) increases, light Absorption (A) increases, linearly.**
- **As Concentration (C) increases, light Transmission (T) decreases,**

exponentially

3. The Spectrophotometer Instrument

All spectrophotometer instruments designed to measure the absorption of radiant energy have the basic components as follows (Figure 4):

1. a stable source of radiant energy (Light);
2. a wavelength selector to isolate a desired wavelength from the source (filter or monochromator);
3. transparent container (cuvette) for the sample and the blank;
4. a radiation detector (phototube) to convert the radiant energy received to a measurable signal; and a readout device that displays the signal from the detector.



Spectrophotometer

Figure 4: Components of a spectrophotometer

The energy source is to provide a stable source of light radiation, whereas the wavelength selector permits separation of radiation of the desired wavelength from other radiation. Light radiation passes through a glass container with sample. The detector measures the energy after it has passed through the sample. The readout device calculates the amount of light absorbed by the sample displays the signal from the detector as absorbance or transmission.

The spectrophotometers, which are used for such measurements may vary from simple and relatively inexpensive colorimeters to highly sophisticated and expensive instruments that automatically scan the ability of a solution to absorb radiation over a wide range of wavelengths and record the results of these measurements.

One instrument cannot be used to measure absorbance at all wavelengths because a given energy source and energy detector is suitable for use over only a limited range of wavelengths.

True linearity between absorbance and concentration according to Beer-Lambert Law requires the use of monochromatic light. In addition, a narrow band of light ensures a greater selectivity since substance with absorption peaks in other close by wavelengths

are less likely to interfere. Further, it increases sensitivity as there is a greatest change in absorbance per increment of change in concentration.

Both filters and monochromators are used to restrict the radiation wavelength. Photometers make use of filters, which function by absorbing large protions of the spectrum while transmitting relatively limited wavelength regions. Spectrophotometers are instruments equipped with monochromators that permit the continuous variation and selection of waveiength. The effective bandwidth of a monochromator that is satisfactory for most applications is about from 1 to 5 nm.

The sample containers, cells or cuvettes, must be fabricated from material that is transparent to radiation in the spectral region of interest. The commonly used materials for different wave length regions are:

Quartz or fused silica:	UV to 2 μm in 1 R
Silicate glass:	Above 350 nm to 2 μm in 1R
Plastic:	visible region
Polished NaCl or AgCl:	Wave lengths longer than 2μm

Cuvettes or cells are provided in pairs that have been carefully matched to make possible the transmission through the solvent and the sample. Accurate spectrophotometric analysis requires the use of good quality, matched cells. These should be regularly checked against one another to detect differences that can arise from scratches, etching and wear. The most common cell path for UV-visible region is 1 cm. For reasons of economy, cylindrical cells are frequently used. Care must be taken to duplicate the position of such cells with respect to the light path; otherwise, variations in path length and in reflection losses will introduce errors.

4. General Measurement Procedures

As explained above, the Beer-Lambert Law forms the basis of the measurement procedure. The amount of light radiation absorbed by a compound is directly related to the concentration of the compound.

The general measurement procedure consists of 5 steps:

1. Prepare samples to make coloured compound
2. Make series of standard solutions of known concentrations and treat them in the same manner as the sample for making coloured compounds
3. Set spectrophotometer to λ of maximum light absorption
4. Measure light absorbance of standards
5. Plot standard curve: Absorbance vs. Concentration, as shown in Figure 5

Once the standard plot is made, it is simple to find the concentration of an unknown sample: Measure the absorption of the unknown, and from the standard plot, read the related concentration (Figure 6).

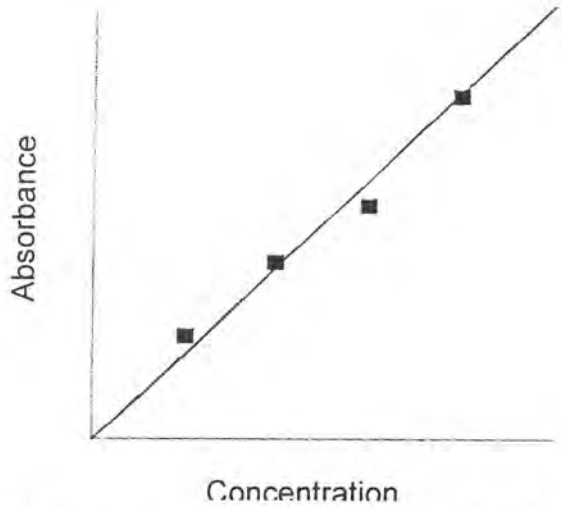


Figure 5: Plot of the standard curve: showing the linear relation between light absorption and concentration of the standards

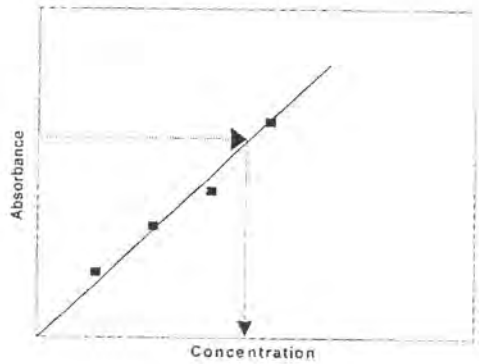


Figure 6: Finding the concentration of an unknown sample from the standard curve.

Due to the fact that the overall composition of the sample is seldom the same as that of the calibration standard, in some cases, the absorption characteristics of the two may differ. Where such discrepancy is suspected, the standard addition approach may be used, Here, a known amount of analyte is added to a second aliquot of the sample. The difference in absorbance is used to calculate the analyte concentration of the sample as illustrated in Example 1.

Example 1

A 25 mL sample after treatment with reagents to generate colour for measurement of phosphate yielded absorbance of 0.428. Addition of 1.00 mL of a solution containing 5.0μg phosphorus to a second 25 mL aliquot and development of colour resulted in an absorbance of 0.517. Calculate μg phosphorus in each mL of sample.

Solution:

Correct absorbance for dilution:

Corrected absorbance = 0.517 (26.0/25.0) = 0.538

Absorbance caused by 5!l9 phosphorus = 0.538 - 0.428 = *0.*110

Therefore, phosphorus in the sample = (5.0/0.11) 0.428
= 19.5µ9, or 19.5/25 = 0.7µ9/mL

OPERATING INSTRUCTIONS FOR SPECTROPHOTOMETER

1. Ensure 230V, 50Hz, single-phase power supply is available in the 3 contact 5A power point.
2. Insert the power cord of the instrument in to a power point.
3. Turn the switch at 'ON" position.
4. Warm up the instrument for 15 minutes.
5. Press %T selector switch.
6. Adjust wavelength control to read the wavelength at which the test is desired.
7. Open the sliding lid of the sample compartment.
8. Turn the filter sliding control at filter position-1 (to set zero adjustment), filter position-2 for below 395nm, filter position-3 for above 395nm and below 600nm,filter position-4 for above 600nm wavelength.
9. Close the sliding lid of the sample compartment.
10. Turn the coarse and fine controls at their maximum and adjust %T control to get 0.00 displayed on the read out with the filter position-1.
11. Keep the blank cuvette at position-1.
12. Keep the sample cuvette at position –2.
13. Adjust 100%T (%T selector switch should be in pressed position) or 0.0 absorbance (O.D selector switch should be in pressed position) using coarse and fine controls knob with blank cuvette.
14. Pull the cuvette position control at position-2.
15. Read out the transmittance/absorbance of the sample.

CHECKING THE PERFORMANCE OF THE SPECTROPHOTOMETER.

1. Preparation of Blank:-

Measure accurately 10 ml of "Anal R" quality HCl of 36-46% concentration. Add it slowly to 400 ml distilled water filled in one litre volumetric flask. Make it up to mark with distilled water and mix it up well.

2. Preparation of sample

Weigh exactly 22.2 gm of "Anal R" quality Cobalt Chloride($CoCl_2$).Transfer into one litre volumetric flask. Dissolve it in 1% Hydrochloric Acid (HCl) and make it up to the mark.

3. Fill the blank (1%HCl) & sample ($COCl_2$ Solution) solution in cuvettes.
4. Perform the steps same as given operating instructions to measure the Transmittance/absorbance at wavelength 480 to 540 nm at 5nm interval.
5. Plot the graph of absorbance versus wavelength. Graph should be in increasing order up to 510-515nm wavelength and then in decreasing order

Precautions

1. Always clean the cells thoroughly and rinse at least once with a portion of the sample, before filling the sample for measurement.
2. Always wipe the exposed surface of the cells dry and free from finger prints, using tissue paper.
3. Clean cells thoroughly immediately after use and prior to use.
4. Do not leave solutions, particularly strong alkali, in the cells for periods more than an hour.
5. Ensure no air bubbles the inner surfaces of the cells.
6. Never use a brush or any tool for cleaning which may scratch the optical surfaces.

Cleaning Method

Take 1gm of Potassium dichromate, add a little distilled water and very slowly add approximately 100ml of Conc.H_2SO_4. Keep the cells in this acidic solution for a maximum period of 12hrs. Wash the cells thoroughly with distilled water before use.

Chapter 12
Electrical conductivity

1 Introduction

As in the case of metallic conductors, electrical current can flow through a solution of an electrolyte also. For metallic conductors: current is carried by electrons, chemical properties of metal are not changed and an increase in temperature increases resistance. The characteristics of current flow in electrolytes in these respects are different: the current is carried by ions, chemical changes occur in the solution and an increase in temperature decreases the resistance.
Electrical conductivity (EC) is a measure of the ability of water to conduct an electric current and depends on:
Concentration of the ions (higher concentration, higher EC)
Temperature of the solution (high temperature, higher EC)
Specific nature of the ions (higher specific ability and higher valence, higher EC)

Conductivity changes with storage time and temperature. The measurement should therefore be made in situ (dipping the electrode in the stream or well water) or in the field directly after sampling. The determination of the electrical conductivity is a rapid and convenient means of estimating the concentration of ions in solution. Since each ion has its own specific ability to conduct current, EC is only an estimate of the total ion concentration.

2 Equations and dimensions

Ohm's law defines the relation between potential (V) and current (I). The resistance (R) is the ratio between V and I:

$$R = \frac{V}{I} \qquad (1)$$

The resistance depends upon the dimensions of the conductor, length, L, in cm, cross-sectional area, A, in cm2 and the specific resistance, p, in ohm.cm, of the conductor:

$$R = P \times \frac{L}{A} \qquad (2)$$

In the present case our interest is in specific conductance or electrical conductivity (which is the preferred term), the reciprocal of specific resistance, K, in 1/ohm.cm or Siemens per centimetre, S/cm, which can be thought of as the conductance offered by 1 cm3 of electrolyte:

$$k = \frac{1}{p} = \frac{L}{A} \times \frac{1}{R} \qquad (3)$$

The resistance of the electrolyte is measured across two plates dipped in the liquid and held at a fixed distance apart in a conductivity cell. The ratio L/A for the cell is called cell constant, Ke, and has the dimensions 1/cm. The value of the constant is determined by measuring the resistance of a standard solution of known conductivity:

$K_c = R_K$ (4)

3 Unit of measurement and reporting

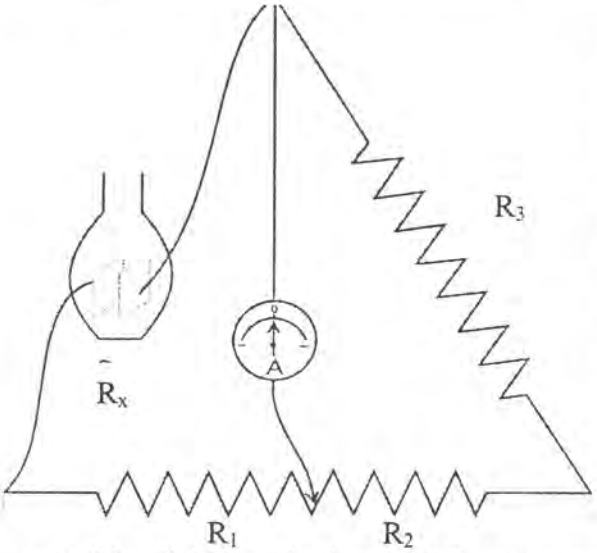
In the international system of units (SI) the electrical conductivity is expressed in Siemens which is the reciprocal of resistance in ohm. The older unit for conductance was mho. Report conductivity as milli Siemens per meter at 25°C ($mS.m^{-1}$). See table for conversions.

Table 1 Conversion table

Multiply	by	To obtain
µS/m	0.001	mS/m
µS/cm	0.1	mS/m
mS/cm	0.01	mS/m
µmho/cm	0.1	mS/m
mmho/cm	100	mS/m

4 Apparatus

An apparatus called a conductivity meter that consists of a conductivity cell and a meter measures conductivity. The conductivity cell consists of two electrodes (platinum plates) rigidly held at a constant distance from each other and are connected by cables to the meter. The meter consists of a Wheatstone bridge circuit as shown in the figure. The source of electric current in the meter applies a potential to the plates and the meter measures the electrical resistance of the solution. In order to avoid change of apparent resistance with time due to chemical reactions (polarisation effect at the electrodes) alternating current is used. Some meters read resistance (ohm) while others read in units of conductivity (milli-Siemens per meter). Platinised electrodes must be in good condition (clean, black-coated) and require replating if readings of the standard solution become erratic. Replating should be done in the laboratory. The cell should always be kept in distilled water when not in use, and thoroughly rinsed in distilled water after measurement.



5 The cell constant (calibration)

The design of the plates in the conductivity cell (size, shape, position and condition),

determines the conductivity measured and is reflected in the so-called cell constant (KG), Typical values for K_c are 0.1 to 2.0. The cell constant can be determined by using the conductivity meter to measure the resistance of a standard solution of 0.0100 molll potassium chloride (KCl). The conductivity of the solution (141.2 mS/m at 25°C) multiplied by the measured resistance gives the value of K_c, Equation 4. The cell constant is subject to slow changes in time, even under ideal conditions. Thus, determination of the cell constant must be done regularly.

6 Temperature correction

Conductivity is highly temperature dependent. Electrolyte conductivity increases with temperature at a rate of 0.0191 mS/m°C for a standard KCl solution of 0.01 OOM.

For natural waters, this temperature coefficient is only approximately the same as that of the standard KCl solution. Thus, the more the sample temperature deviates from 25°C the greater the uncertainty in applying the temperature correction. Always record the temperature of a sample (±0.1°C) and report the measured conductivity at 25°C (using a temperature coefficient of 0.0191 mS/m°C)

Most of the modern conductivity meters have a facility to calculate the specific conductivity at 25°C using a built in temperature compensation from 0 to 60°C. The compensation can be manual (measure temperature separately and adjust meter to this) or automatic (there is a temperature electrode connected to the meter).

7 Conductivity factor for different ions

Current is carried by both cations and anions, but to a different degree. The conductivity due to divalent cations is more than that of mono-valent cations. However, it is not true for anions. The conductivity factors for major ions present in water are listed below.

Table 2 Conductivity Factors for ions commonly found in water

Ion	**Conductivity Factor *µS/cm* per mg/L**
Cations	
Ca^{2+}	2.60
Mg^{2+}	3.82
K^{+}	1.84
Na+	2.13
Anions	
$HC0_3$	0.715
Cl	2.14
SO_4^{2-}	1.54
$N0_3$	1.15

The conductivity of a water sample can be approximated using the following relationship

$EC = \Sigma (C, X f,)$

in which

EC = electrical conductivity, µS/ cm
C_i = concentration of ionic specie i in solution, mg / L
f_i = conductivity factor for ionic specie i

Example 1

Given the following analysis of a water sample, estimate the EC value in µ S/cm and mS/m.

Cations: Ca^{2+} = 85.0 mg/L, Mg^{2+} = 43.0 mg/L, K^+ = 2.9 *mg/L,* Na^+ = 92.0 mg/L
Anions: HCO_3-=362.0 mg/L, Cr=131.0 mg/L, SO_4^{2-}=89.0 mg/L, NO_3-=20.0 mg/L Calculate the electrical conductivity of each ion using the data given in Table 3.

Table 3 Ion specific conductivity's

Ion	Cone. mg/L	Factor µS/cm per mg/L	Conductivity µS/cm
Ca^{2+}	85.0	2.60	221.0
Mg^{2+}	43.0	3.82	164.3
K^+	2.9	1.84	5.3
Na^+	92.0	2.13	196.0
HCO_3	362.0	0.716	258.8
Cl	131.0	2.14	280.3
SO_4^{2-}	89.0	1.54	137.1
NO_3	20.0	1.15	23.0
			Total 1285.8

Electrical Conductivity = 1285.8 *µS/cm* = 1285.8 *X 0.1* = 128.58 *mS/m* (Table 1).

8 Use of EC measurement

- **Check purity of distilled or de-ionised water**

Table 4 Gradation of water for laboratory use.

Gradation of Water	Use of water	EC (mS/m)
Type I	use at detection limit of method	<0.01
Type II	routine quantitative analysis	<0.1
Type III	washing and qualitative analysis	<1

- **Relations with many individual constituents and TDS can be established.**
  The relationship between TDS (mg/L) and EC (µS/cm) is often described by a constant, that varies according to chemical composition: TDS = A x EC, where A is in the range of 0.55 to 0.9. Typically the constant is high for chloride-rich waters and low for sulphaterich waters.

- **Check deterioration of samples in time (effect of storage)**
  If EC is checked at time of sampling and again prior to analysis in the laboratory, the change in EC is a measure for the 'freshness' of the sample.

Example 2

For the water sample given in the example in 0, *calculate TDS and the corresponding constant 'A'.*

Ion	Cone. Mg/L
Ca^{2+}	85.0
Mg^{2+}	43.0
K^{+}	2.9
Na^{+}	92.0
$HC0_3$	362.0
Cl	131.0
SO_4^{2-}	89.0
$N0_3^{-}$	20.0
Σ = 824.9	

TD8 in the sample = 824.9 mg/L. EC value = 1285.8 µS/cm.

TDS = A x EC
824.9 = A x 1285.8
= 0.64

OPERATION OF CONDUCTIVITY METER

Measurement of the conductivity

1.Connect the conductivity electrode to the measuring instrument.
2.Press the < Φ>key. (display test appears briefly on the display, after this, the measuring instrument automatically switches to the measuring mode.)
3.Select the parameter (TDS, Salinity, Conductivity) by pressing <M>key.
4. Immerse the electrode in the water sample.
5. Press <AR> Key to activate auto read.
6. Press <Run/Enter> Key to start the auto read measurement, AR flashes on the display until a stable measured value is reached, this can be terminated at any time with <Run/Enter> Key.

Storing the data

1.Press the <STO>key in the measuring mode (display number with the number of the next free memory location).
2. Press <Run/Enter>key.
3. Enter the ID number with <∇ >< Δ>.
4.Terminate the save with <Run/Enter>key.

To see the data memory

1Press <RCL>Key.(display SEr disp)
2.Press <Run/Enter>key (display number at which data store)
3.Press <Run/Enter>key (display identification number).
4.Press <Run/Enter>key (display day, month)
5.Press <Run/Enter>key (display time)
6.Press <M>key to return in measuring mode.

Calibration

1.Connect the conductivity Electrode to the measuring instrument.
2.Immerse the electrode in the electrolyte solution provided with the instrument.
2.Press the <Cal>in the measuring mode (display Cell).
3. Press <Run/Enter>key (display CAL and cell constant value ,it should be 0.450-0.500Cm^{-1})
note :- At this point ,this procedure can be terminated with<M>.

Precautions

1. Always keep the electrode dry before and after use with absorbent paper.
Need to Calibrate after a fixed interval.

Chapter 13
Measurement of hydrogen ion concentration (PH)

1. General

pH is a way of expressing the hydrogen ion concentration in water. It is related to the acidic or alkaline nature of water. Consideration of hydrogen ion concentration is important in almost all uses of water. In particular, pH balance is important in maintaining desirable aquatic ecological conditions in natural waters. pH is also maintained at various levels for efficient operation of water and wastewater treatment systems such as coagulation, disinfecting, softening, anaerobic decomposition of wastes, etc. The pH of most natural waters lies between 6.5 and 8.

2. The pH scale

Pure water dissociates to yield 10^{-7} moles/L of H^+ at 25 °C:

$$H_2O \Leftrightarrow H^+ + OH^- \qquad (1)$$

Since water dissociates to produce one OH^- ion for each W ion. It is obvious that 10^{-7} OHions are produced simultaneously.

The product of [H^-] and [OH^-] always remains constant even if the value for one of the species changes

$$[H^+] \times [OH] = 10^{-14} \qquad (2)$$

The large bracket sign, [ ], indicates molar concentration.

The concentration of H^- ions can be increased when compounds are added which release W ions such as H_2SO_4:

$$H_2SO_4 \longrightarrow 2H^+ SO_4^{2-} \qquad (3)$$

Or preferentially combine with OH- ions when added to water, such as $FeCl_3$:

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ 3Cl^- \qquad (4)$$

Note that in either case the product of *[W]* and [OH-] ions remains constant at 10^{-14}

Likewise the concentration of W ions can be decreased when compounds are added which release OH^- ions, such as NaOH, or preferentially combine with W ions, such as Na_2CO_3.
Expression of the molar concentration of hydrogen ions is rather cumbersome because of

the extremely small values and large variations. To overcome this difficulty, the concentration is expressed in terms of pH value, which is negative logarithm of the concentration in moles/L.

$$pH = -\log [H^+] \quad (5)$$

or

$$[H^+] = 10^{-pH} \quad (6)$$

Thus the pH value of a sample of water containing $10^{-7.5}$ moles/L H^+ is 7.5.
Since the product of $[H^+]$ and $[OH^-]$ is always a constant, Eq. (2) becomes

$$\log[H^+] + \log[OH] = -14$$

Or

$$-\log[H^+] - \log [OH] = +14 \quad (7)$$

The pH scale is usually represented as ranging from 0 to 14, with pH 7 at 25 °C representing neutrality. Acid conditions increase as pH values decrease and alkaline conditions increase as pH values increase.

Acid range					Neutral					Alkaline range			
1	2	3	4	5	6	7	8	9	10	11	12	13	14

3. Calculating pH

Example calculation

Calculate the pH value for the following cases:

A: $[H^+]$= a.0.001
b.0.00005 and

B: $[OH^-]$ = a 10^{-8}
b. 0.00005 and
c.0.00001

A: $[H^+]$ a. 0.0001 pH= -log 10-3 =3
A. 0.0005 pH= -long 0.00005= -log (5 x10^{-5})= 0.7 +5=4.3

B:$[OH^-]$ a. 10-8 $[H^+] \times 10^{-8} = 10^{-14}$, or $[H^+]=10^{-6}$
Therefore pH=6
b. 0.00005 $-\log[H^+]-\log [OH^-]=14$
Therefore pH=14-4.3 =9.7
c. 0.00001 $pH=14 + \log 10^{-5}=14^{-5}=9$

4. pH indicators

A number of naturally occurring or synthetic organic compounds undergo definite colour changes in well-defined pH ranges. A number of indicators that are useful for various pH ranges are listed in Table 1. The indicators assume different hues within the specified pH range. These are used as liquid solutions or some as pH papers. The change in colour occurs over a wide range of pH change and therefore pH value cannot be measured accurately. Further, the turbidity and colour of the sample may cause interference.

Table 1

Indicator	Acid colour	Base colour	pH range
Methyl orange	Red	Yellow orange	3.1-4.6
Methyl red	Red	Yellow	4.4-6.2
Litmus	Red	Blue	4.5-8.3
Thymol blue	Yellow	Blue	8.0-9.6
Phenolphthalein	Colourless	Pink	8.2-9.8
Alizarin yellow	Yellow	Lilac	10.1-11.1

5. pH meter

The use of colour indicators for pH measurements has, to some extent, been superseded by development of glass electrode. pH meters employing glass-indicating electrodes and saturated calomel reference electrodes are now commonly used. Such meters are capable of measuring pH within $\pm$ 0.1pH unit. The electrodes, connected to the pH meters are immersed in the sample and the meter measures the potential developed at the glass electrode due to hydrogen ion concentration in the sample and displays it directly in pH units. The pH meters are also equipped with a temperature-compensation adjustment.

The electrodes should be carefully handled and should not be scratched by butting against the sides of the beaker containing the sample. Follow the manufacturer's instructions for their care during storage and use. For short-term storage, the glass electrode may be left immersed in pH 4 buffer solution., Saturated KGl is preferred for the reference electrode. The glass electrode needs to be soaked in water for at least 12 hours before it is used for pH measurement.

Buffer solutions & instrument calibration

pH meters have to be calibrated against solutions of known pH values. Standard buffers are used for this purpose. Buffers are solutions of chemicals of known pH which do not

change their pH value upon dilution and resist change of pH when small amounts of acid or alkali are added to them. Buffer solutions usually contain mixtures of weak acids and their salts (conjugate bases) or weak bases and their salts (conjugate acids). Buffer has importance for life forms that usually can survive only within a narrow pH range. Table 2 gives the composition of some commonly used buffers. Buffers of different pH values are also available commercially.

Table 2 Buffer solutions of known pH

S. No	Buffer solution	pH at 25°C	Amount of salt to be dissolved in 1000 ml freshly boiled and cooled and cooled distilled water
1.	0.05 M potassium hydrogen phthalate	4.00	10.12 g $KHCaH_4O_4$
2.	0.025 M potassium dihydrogen phosphate + 0.025 M disodium hydrogen phosphate	6.86	3.387 g KH_2PO_4 and 3.533 g Na_2HPO_4
3.	0.01 M sodium borate decahydrate	9.18	3.80 g $Na_2B_4O_7.10\ H_2O$

It is a good practice to calibrate the pH meter using two buffers. After calibrating with an initial buffer, use a second buffer within 2 pH units of the sample pH.

OPERATION OF THE pH METER

How to measure the pH

1. Connect the pH electrode & temperature sensor to the measuring instrument.
2. Press the on/off Key.(display test appears briefly on the display)
3. Select pH value or redox voltage (mv) with <M>.
4. Immerse the pH electrode in water sample .
5. Press <AR>to switch on the drift control. Wait until measured value is stable and AR stops flashing.
6. To cancel auto read at any time press <Run/Enter>.

Storing the data

1.Press <STO>Key in the measuring mode(display No. with the number of the next free memory location.

2. Press <Run/Enter>.

3. Enter the Identification number with < ∇> <Δ>.

4. Terminate the save with <Run/Enter>.

How to see data memory

1. Press the <RCL> key in the measuring mode.(display Sto disp)
2. Press <Run/Enter>key (display number at which data store)
3. Press <Run/Enter>key(display identification number)
4. Press <Run/Enter>key (display day .month)
5. Press <Run/Enter>key (display time)
6. Press <M>key to return in measuring mode.

Calibration

1. The pH electrode to the measuring instrument.
2. Press the <Cal>key repeatedly untill the display Ct1 and the function display Auto Cal TEC appears. The sensor symbol displays the evaluation of the last calibration.
3. Immerse the pH electrode in to the first buffer solution (pH-7.0)
4. Press <Run/Enter>key.(the auto read measurement begins. If the measured value is stable, Ct2 appears.

Note:--At this point , the auto cal TEC calibration can be terminated with <M>.

1. Immerse the two pH electrode in the second buffer solution to continue.
2. Press <Run/Enter>key(the auto read measurement begins.) If the measured value is stable, the instrument displays the value of the slope and the evaluation of the two point calibration.
3. Press<Run/Enter>key.(the instrument displays the value of the asymmetry)
4. Switch to the measuring mode with<M>.
5. To set calibration interval, while pressing the <M>key, press <ON/OFF>Key.(display CAL disp)
6. Press <Run/Enter>key.(display time of calibration display)
7. Set the interval of Calibration with <Δ > <∇ >.

Precautions

1. Always keep the electrode wet(with electrolyte in the cap of electrode),if you use it after 2 or 3 days interval.
2. Keep it in ordinary water if you use continuously.
3. Clean properly with absorbent paper before and after use.
4. Need to Calibrate after a fixed interval.

Chapter 14
High-Volume Sampler

MONITORING OF PARTICULATES IN AMBIENT AIR

Introduction:

Air-borne particulate matter is an ensemble of solid particles suspended and dispersed in air. The properties of these particles vary in terms of chemical composition, morphology (size/shape) optical parameters (colour/light scattering), and electrical characteristics (charge, resistance). Particles, which in general are non spherical are classified in terms of their aerodynamic diameter. This is defined as the diameter of a sphere of unit density (i.e. 1.0gm/cm^3, equivalent to that of water).

In ambient air dust particles have size range from some tens of nanometer to some hundreds of micrometer (µm). In ambient air SPM has bimodal mass distribution with respect to size whose shape depends on the predominant physical and chemical formation processes of particles. Tables 1 gives a brief definitions of the various particle size convention adopted by International organization for standardization.

S. No.	Particulates Term	Definitions
1.	Total Airborne Particles	All particles surrounded by air in a given volume of air Size range of particles is few nanometer to several hundred microns (µm).
2.	Suspended Particulate Metter	Is an estimate of total air borne particle mass measured by HVS. Particle size upto 100 µm.
3.	Inhalable Fraction	Is the mass fraction of total air borne particles which is inhaled through nose and mouth. Particle size upto 100µm.
4.	(i) Thoracic Fraction	Is the mass fraction of inhaled particles which penetrate beyond larynx (size range upto 10 µm)
	(ii) Extra thoracic Fraction	The mass fraction of inhaled particles failing to penetrate beyond larynx (example pollens)
5.	Respirable Fraction (Alveolar Fraction)	The mass fraction of inhaled particles which penetrates to the un ciliated air ways (Particle size range upto 2.5µm)

Measurement of TSPM and Respirable Particulate Mater (Thoracic Fraction(Pm10)) using High Volume Respirable Dust Sampler Equipped with Cyclone.

Pm 10 and TSPM are measured by passing air at flow rate of about 1.1 m^3/min through high efficiency cyclone which retains the dust particles greater then 10 micron size and allow only fines (less than 10 micron particles) to reach at glass microfibre filter where these particles are accumulated. The instrument provides instantaneous flow rate and on time for calculation of air volume passed through the filter. Amount of particulates collected on the filter is determined by measuring the change in weight of the cyclone cup and filter paper.

The passage of air entering in the cyclone is designed to prevent heavier settle able particles from reaching in the cyclone.

Envirotech RDS has following unique features for quality reliable results with user conveniences.

- Unique flow measurement system using orifice plate directly calibrated in m^3/min. This is incorporated in filter holder casting which eliminates leakage while sampling and correct flow reading are obtained on provided manometer.
- Cabinet is annodized to withstand weathering effects. Thus unit can be operated in corrosive environment without any unwanted fears.
- A brushless and low noise pump is provided which reduces operation cost and maintenance problems. Thus instrument can be operated in residential and sensitive areas without hindrance.
- Manometer assembly has been shifted in top portion of the machine for better readability.
- MCB switch has been provided at the place of fuse and toggle switch for better safety and convenience.
- Pump is equipped with induction type motor which has capability to maintain its rpm at variable input voltage. Thus flow is not changing with change in input voltage.

Detailed method for monitoring of Respirable Particulate matter (Pm10) has been given in standard method enclosed as Appendix-1

Monitoring of SPM can also be done using Envirotech RDS APM 460NL if quantity of dust collected in cyclone cup is estimated. A clean pre weighed cyclone cup need to be fitted while setting filter paper for finding out dust accumulated in the cup during sampling. All steps like conditioning before post weighing and calculation of the concentration need to be followed for finding out NRSPM (non Respirable Suspended Particulate Matter particles size above 10 micron). To find out TSPM concentration Pm10 and NRSPM need to be added. It is important to collect dust from bottom of the cyclone hopper carefully in cyclone cup. A small brush has been provided for dislodging particles from hopper. Some observed concentration of TSPM measured by co-locating Respirable Dust Sampler and normal HVS and operating them simultaneously for equal sampling durations. Obtained data (Appendix-II) confirms that using RDS one can measure Pm10 and TSPM within experimental errors.

Overall accuracy of particulates (Pm10 and TSPM) measurements using RDS is within $\pm$5%.

If two RDS are operated simultaneously by co-locating them for equal duration obtained results (Appendix-II) are found within these tolerances.

In following sections important precautions are described to be followed for reliable repeatable results. For further details on instruments parts and its operation procedure one may refer operation manual supplied with RDS Envirotech APM 460 NL.

Selection of Sampling Site

Monitoring site need to be 3-10m high from ground level. In present project where pollutants are expected from long distances through upper atmosphere. It is desirable to keep instrument at a height of about 8-10m. This shall result elimination of local activities contribution if any. To get representative sample sampler must not positioned near a wall or other obstruction that would prevent free airflow. In excessively turbulent conditions or in the presence of strong surface winds or otherwise inclement weather, the sampling rate is likely to decrease rapidly and perhaps in a non-linear fashion due to filter choking. If the sampler is operated continuously, day-to-day variations in the measurement are expected due to varying meteorological conditions and changing atmospheric phenomena, like wind speed and direction, dispersion- diffusion, etc. beside impact of

emission sources.

Selection of Filter Medium:

For most cases interest is limited to a gravimetric determination of the Pm 10 total suspended particulate concentration Glass Micro Fibre filters having low resistance to air flow, low affinity for moisture and 99% collection efficiency for particles of 0.3 microns or larger size are suitable. However, where further analysis, of the particulates is to be attempted, to detect specific elements/radicals, care should be taken to choose special filter medium having a low background concentration of the substances of interest. For instance, special grades of Glass Microfibre filters like Whatman EPM2000 are available which have a controlled and a low known concentration of metals like Iron, Zinc, Cadmium, Lead, Arsenic, Nickel, etc.

Preparing the Filter

Prior to use, expose each filter to a light source and inspect for pinhole, particles and other imperfections. Filters with visible defects should not be used. A small brush is often used to remove stray particles adhering to the surface of new filters. Always handle filter papers from their edges and do not crease or fold the filter prior to use

Both blank and samples should be conditioned in a desiccator with active desiccant at 20 - 25°C should have humidity below 50% R.H. for at least 16 hours prior to weighing. It is usual to put an identification number and date of sampling on the filters. Weigh the filters to the nearest milligram (accurate upto 0.1 mg for RDS filters and'cup) and record the weight and filters identification number in data sheet (Appendix-III). Ensure keeping a perforated plastic bottle filled with active silica zel in weighing chamber for minimizing impact of moisture during weighing.

Installation of Filter

Install or remove filter only when the sampler is off. The numbered and pre weighed filter is always kept with its rough side up. This increases the collection efficiency of the filter.

The filter is placed in its proper position on the top of wire mesh. The sampler is started before putting back the top cover. This prevents the filter to shift from its place. As a result., any undesirable leakage from top is prevented. The top cover is not to be under tightened as it will give way to leakage and over tightening will damage the rubber gasket and filter. It is not very difficult to ascertain the extent to which the top cover is to be tightened but, one learns through practice only. A very light application of talcum powder on the rubber gasket prevents the filter from sticking to it. Ensure that top cover which has polarity need to be fitted such so that 'Envirotech' printed side is towards front side (side where manometer assembly is fitted)

Recording Correct Flow rates

Manometer Assembly

For recording correct flow rate ensure zero level of the water in manometer tube. Always use distilled water for filling in the tube and every fortnightly water must be changed. Least count of manometer scale is 0.01 m^3/min. Care is needed in taking reading always read lower meniscus of water level in the monometer tube. Manometer scale can be shifted up or down by loosening mounting screws of the scale to adjust zero level. Typical view of manometer scale is shown in
Appendix-V.

Rotameter Assembly

Ensure that no solids are deposited in the nozzle and tube of the rotameter Float must move freely in the rotameter tube. To record correct flow level of widest portion of float is recorded. A typical rotameter has been shown in Appendix-V with marking which part of the float is required to be set and read.

Time Totalizer

A time totalizer unit fitted in the machine uses a clock motor to drive a geared numerical display. The unit is wired so that it operates only when blower receives power. Hence its display indicates true time for which the sampler has sampled atmospheric air. It performs two important functions.

(i) It keeps a check on actual sampling time when instrument is operated.

(ii) It facilitates timely preventive maintenance.

Time totalizer reading should be noted before and after each air sampling so that exact duration of sampling can be worked out.

Sampling calculation for finding out Pm10 and TSPM concentration using Envirotech Respirable Dust Sampler APM 460NL has been shown in Appendix- IV

PRECAUTIONS TO BE FOLLOWED DURING SAMPLING FOR RELIABLE DATA COLLECTION

1. Filter paper need to be inspected for pin holes
2. Filter conditioning need to be done at 20-25°Ctemperature and less than 50% Humidity.
3. Never fold filter completely.
4. Do not touch filters by dirty hands.
5. Under take regular cleaning of key components of the machine.
6. Perform leak check of the instrument before starting the sample.
7. Read operation manual of the instrument completely before starting monitoring.
8. Ensure stable power supply to the machine. Do not leave loose contact of supply wire to the machine.
9. Electrical cable used with extension board must be with copper wire, which can take load upto 15 amps.
10. Always fill up distilled water in manometer assembly.
11. Manometer tube water need to be filled up fresh every fortnightly.
12. Do not switch on and off machine using Timer Switch.
13. Clean impinger rotameters regularly and also clean manifold once in two months.
14. Don not take flow reading immediately after switching on the machine. Give 5 minute for flow stabilization and for heat up the blower components.
15. Always attach a new weighed cyclone cup with every filter change.
16. Do not run machine during rains.
17. Operate machine at a height of 8-10 meter and try to do repeat monitorings at equal height always.
18. If machine is not expected to be operated within 48 hrs drain out the manometer water and store machine with water in the manometer tank.

IMPORTANT INSTRUCTIONS FOR OPERATION OF RESPIRABLE DUST SAMPLER APM 460 NL

CHECK

RESPIRABLE DUST SAMPLER ENVIROTECH APM 460 NL

- Filter paper is properly placed on the wire mesh.
- Initial water level in manometer tube is at zero level and there is no residue.
- Timer has been set properly after setting reset switch of timer.
- Hose connected to blower is tight
- Top cover is sufficiently tightened.
- Cyclone is properly cleaned and cup is fitted properly.

GASEOUS ATTACHMENT APM 411

- Ice has been put in the ice tray.
- Impingers are properly greased after cleaning.
- Float in rotameter is freely moving.

DO'S

- Change manometer water every fortnightly
- Use only distilled water for filling in manometer tube.
- Ensure removal of air bubbles from water column if any.
- Change deformed Silicon Tube, 'O' Rings 6 monthly.

DONT 'S

- Clean the blower with moisture-laden compressed air.
- Operate machine while it is raining.
- Operate machine without filter paper.

MAINTAINANCE

The APM 460 NL Respirable Dust Sampler has few moving parts that would require maintenance. The flow metering is performed by a completely static orifice plate assembly requiring no significant attentions. However, for trouble free operation the manometer assembly used to indicate the flow rate must be periodically cleaned and deformed 'O' rings are replaced periodically.

MAINTENANCE OF THE MANOMETER ASSEMBLY :

The manometer assembly uses distilled water as a manometer fluid. With time the water acquires residues and a precipitate forms which tends to clog the nozzles connecting the manometer tank to the manometer tube To remove the precipitate and other deposits the manometer must be flushed out periodically (at least once in three months). If the instrument is expected to remain in disuse for two weeks or more it is recommended that the water be drained out fro the manometer tank to avoid formation of the precipitate. To flush and clean the manometer assembly follow the steps given below:

- Observe the polarity of the PVC pipes connecting the manometer to the pressure taps of the Orifice Plate. The glass tube of the manometer is connector to the lower nozzle while the manometer tank is connected to the upper nozzle of the filter adaptor casting. Remove both the PVC pipes from the orifice plate pressure taps.
- Hold the pipe from the glass tube pointing downwards and away from the instrument and blow into the pipe connected to the tank. The old water residues will be drained from the system.
- Refill the manometer with fresh distilled water (through the filling plug) and drain it as above. Repeat the process several times to thoroughly flush out any residues.
- Re-connect the PVC pipes to their respective places on the filter adaptor casting and fill fresh distilled water prior to use of the instrument.

Preventive Maintenance of Blower Assembly:

Standard Regenerative blower has been used in your machine for Sucking of ambient air through glass microfibre filter. A induction type brushless motor with high rpm (2850 at 50

Hz) has been coupled with specially designed impeller. Thus this regenerative blower is one type of non positive displacement pump. Due to special blade and housing configuration, as regenerative blower impeller rotates, centrifugal force moves the air molecules from root of the blade to the tip of the blade. Leaving the blade tip, the air flows around the housing countor and back down to the root of succeeding blade, where flow pattern is repeated. Impeller designed flow of air has been shown in the DRG 460NL-V.1 This action provide a quasi staging effect to increase pressure differential capability. The speed of the rotating impeller determines the degree of the pressure change.

Overall it can be said that the blower is heart of the machine need to be maintained critically. Exploded view of blower has been shown in DRG 460 NL V.2. which clearly reveals the various parts of blower and their order of fitment. Ordering information for various parts are given on DRG 460 NL-V.2 and in Annexure III.

Following are blower specification

Model	Motor Speed	RPM	Max.Vac.(inch)	HP	KW	Weight Kg.
R-4110-2	220-240-50-1	2850	34	0.6	0.45	18.6

Sound Level – 64 dB(A) Max at 50 Hz

Temperature of operation –29 to 40°C

Humidity for operation 0- 100% Non condensing

Warning

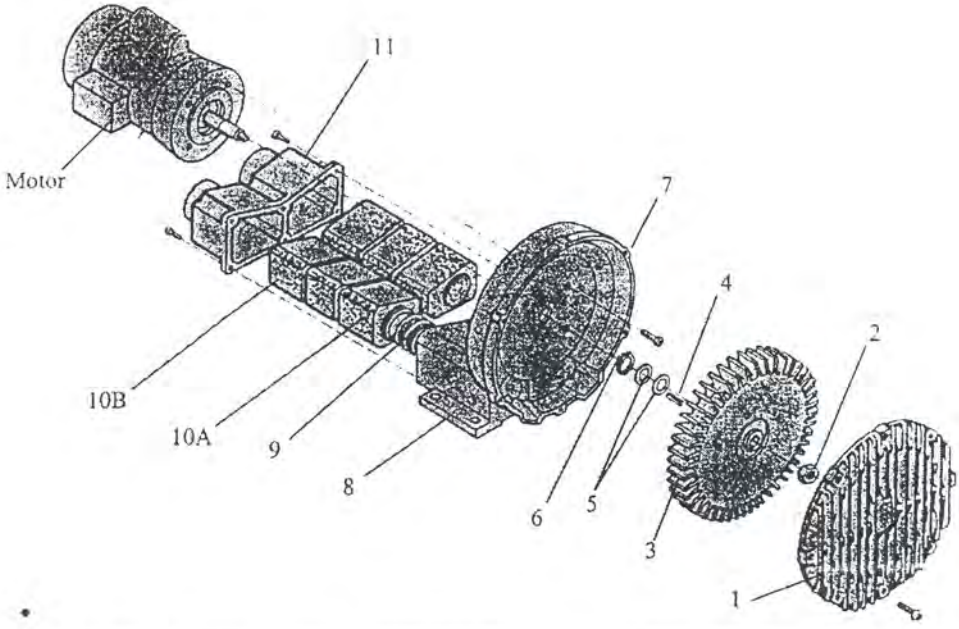
Power must be de-energized and disconnected before servicing. Be sure all rotating parts have stopped. Electric shock or severe cuts can result if hazard is ignored.

Noise-absorbing foam used in mufflers needs to be periodically replaced. The electric motor and blower also need periodic cleaning to remove accumulated dust and dirt. If they are not cleaned, this can result in excessive vibration, an increase in temperature, or can reduce service life of the blower. Initial inspection is suggested at 8000 hours, then user should determine frequency.

An increase in differential pressure across an inlet filter indicates its getting clogged. Clean inlet air filter as often as needed, blowing down against current to clean it. Change cartridge when cleaning no longer gets cartridge clean.

A dirty cartridge causes a high intake resistance resulting in an increase of differential pressure, absorbed power, and working temperature.

The motor bearing of your blower motor are greased for long life. To re-grease these bearings clean tip of grease gun and apply grease to fitting.



Ref No.	Description	Part Qty	R4110-2
1.	Cover	1	AJ 101D
2.	Stopnut	1	BC 181
3.	Impeller	1	AJ 102 D
4.	Square Key	1	AB 136 D
5.	Shim Spacer	As Req.	AJ 109
6.	Retaining Ring	1	AJ 149
7.	Housing	1	AJ 103 DR
8.	Muffler Box	1	—
9.	Spring	2	AJ 113 DR
10A.	Foam	As Req.	(4) AJ113DR
10B	Foam	2	AJ112DR
11	Muffler Extension	1	AJ106 DQ

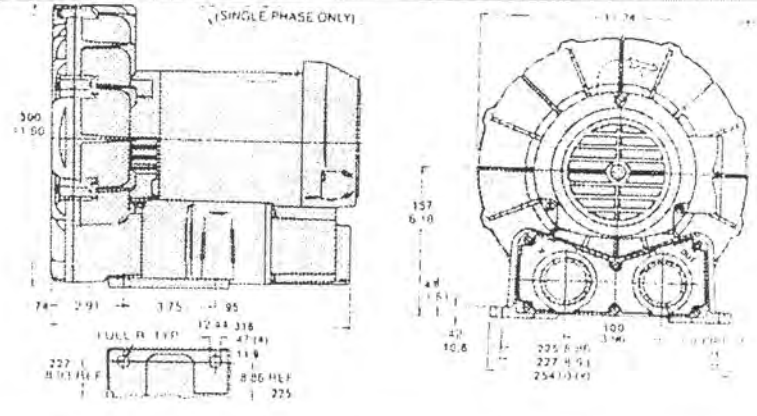


Figure- Exploded view of Blower with ordering information's and size of blower

460 NLV.2

Appendix I

Ambient Air Quality Monitoring Programme
Dust Concentration Monitored During Training Course by Participants

Location - A-271, Okhla Ind. Area, Ph.- I, New Delhi , Type - 12 Hourly

SN	Dated	Instruments	Concentration (µg/m³)			
			RPM	NRPM	TSPM	Pm 2.5
1.	13-14/03/2001 (Night)	RDS - 460 RDS - 460 NL RDS - 460 DX HVS FPS - 550	186 189 182 -	271 267 280 -	457 456 462 482	- - - - -
2	14/03/2001 (Day)	RDS - 460 RDS - 460 NL RDS - 460 DX HVS FPS - 550	205 Sample 211	809 Destroyed 830	1014 ---------- 1041 1093	- ---------- - - 100(24 hourly)
3	14-15/03/2001 (Night)	RDS - 460 RDS - 460 NL RDS - 460 DX HVS FPS - 550	134 124 113 -	249 261 269 -	373 385 383 390	- - -
4	15/03/2001 (Day)	RDS - 460 RDS - 460 NL RDS - 460 DX HVS FPS - 550	97 96 88 -	299 300 305 -	396 396 413 417	- - - - 36(24 hourly)

Monitorings were carried out using conditioned GF/A grade Whatman make filter papers. Four instruments were operated simultaneously at roof top of the building. All individuals undertook monitoring using 4 different models of Samplers.

Sl. NO.	Name of the Participant	Signature
1.	Shri Ranjan Bordoloi Assam State Pollution Control Board	R Bordoloi
2	Shri Hiten Sarma Assam State Pollution Control Board	Hsarma
3.	Shri Bantehsonglang Blahwar Meghalaya State Pollution Control Board	
4	Shri Surjya Sankar Mishra Regional Office of Orissa State Pollution Control Board	Surjya Sankar
5	Mr. Tiwari Vasu 'PAMS' Division Central Pollution Control Board	

AMBIENT AIR QUALITY MONITORING

E.C.R.&D.
New Delhi

Station			
Instrument used and Sl. No.			
Filter Paper No.		Dust Cup No.	

Particulars	Initial	Final
Date		
Time of Sampling (hrs.)		
Manometer Reading (m^3/min)		
Time totalizer reading (hrs.)		
Wt. of filter paper (gm)		
Wt. of Dust Cup (gm)		
Rotametere Reading (1pm)	SO_2	SO_2
	NO_x	NO_x
Absorbing Reagent taken for sampling (ml)	SO_2	SO_2
	NO_x	NO_x
Loss of Water due to evaporation (ml)	SO_2	NO_x
Absorbance value	SO_2	NO_x

1) Cloud Cover or general weather .....

2) Any activity that may cause change in values .....

3) Ambient temperature
Start ..... End .....

PM_{10} ($\mu g/m^3$)		NRSPM ($\mu g/m^3$)		TSPM ($\mu g/m^3$)		SO_2 ($\mu g/m^3$)		NO_x ($\mu g/m^3$)	

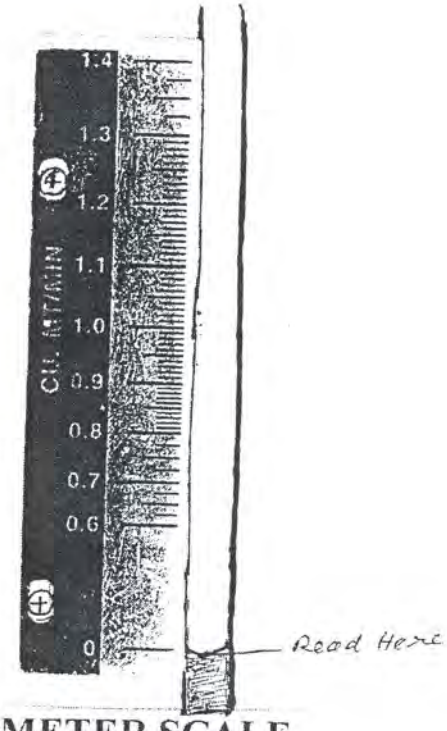
Name & Signature .....

SAMPLE CALCULATION FOR RESPIRABLE PARTICULATE MATTER AND TOTAL SUSPENDED PARTICULATE MATTER USING ENVIROTECH RESPIRABLE DUST SAMPLER APM 460/460DX/460NL/460BL

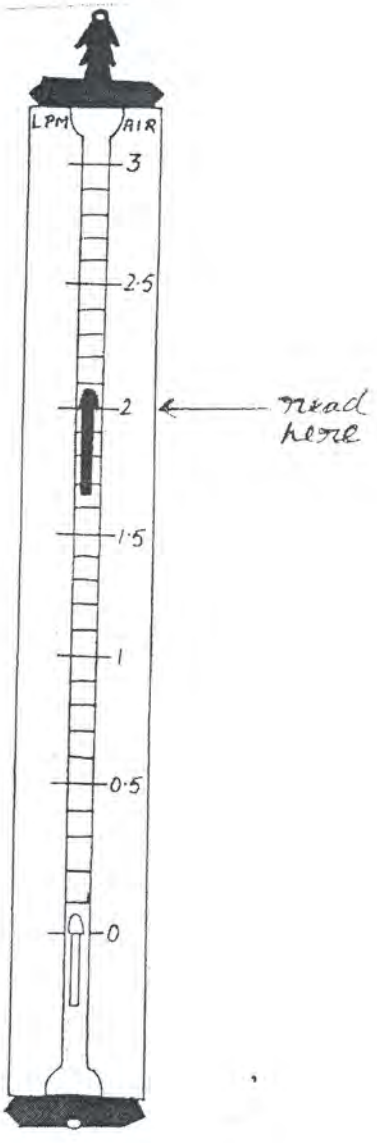
S. No.	Record Following Data	Assumed
A. i)	Initial Manometer Reading	1.1m^3/min.
ii)	Final Manometer Reading	0.9m^3/min.
B. i)	Initial Filter Paper Weight	2.8538 gm.
ii)	Final Filter Paper Weight	3.0857 gm.
C. i)	Initial Cyclone Cup Weight	16.8354 gm.
ii)	Final Cyclone Cup Weight	17.0359 gm.
D. i)	Initial Time Totalizer Reading	53.67 hrs.
ii)	Final Time Totalizer Reading	73.39 hrs.
E.	Average Flow rate $= \left(\frac{A(i) + A(ii)}{2} = \frac{1.1 + 0.9}{2} \right)$	1.0m^3/min.
F.	Total on time of Machine = [D(ii)-D(i) X 60= (73.39-53.67) X60]	1183.2 min.
G.	Respirable Dust accumulated on Filter = [B (ii)-B(i)=3.0857-2.8538]	0.2319gm.
H.	Non- Respirable dust accumulated in Cyclone cup= [C (ii)-C(i)=17.0359-16.8354]	0.2005 gm.
I.	Total Volume of air passed through Cyclone/Filter Paper = [E x F = 1.0 x 1183.2]	1183.2 m^3
J.	Respirable Particulate Matter Concentration= $\left(\frac{G \times 10^6}{(I)} = \frac{0.2319 \times 10^6}{1183.2} \right)$	196.1 ug/m^3
K.	Non-Respirable Particulate Matter Concentration= $\left(\frac{(H) \times 10^6}{(I)} = \frac{0.2005 \times 10^6}{1183.2} \right)$	169.5 mg/m^3
L.	Total Suspended Particulate Mater Concentration= [J + K = 195.9 + 169.5]	365.4 µg/m^3

Note: Initial Readings= Readings taken at time of starting the sample
Final Readings= Readings taken before switching of the sampler after sampling

Appendix V



MANOMETER SCALE



ROTAMETER

Activity Matrix for Calibration of Equipment : SPM Monitoring

Equipment	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical balance	Use 3 to 5 standard weights covering normal range of filter weights; weight difference within 1 mg	Gravimetric test; calibration at installation and periodic checks	Have balance maintained and calibrated by manufacturer
Relative humidity indicator	Indicator reading = Psychrometer reading $\pm$ 6%	Comparison with reading of wet bulb/dry bulb psychrometer receipt and every 6 monthly after words	Adjust or replace to attain acceptance limits
On-off timer *	$\pm$ 15 min/24 h	Check at purchase and quarterly with elapse-time meter	Adjust, and repeat test
Elapsed-time meter*	$\pm$ 2 min/ 24 h	Standard timepiece of known accuracy at receipt and every 6 monthly afterwards	Adjust or replace time indicator to attain acceptance limits
Orifice calibration unit	Difference in flowrate <$\pm$4 %	Rootsmeter at installation and after words yearly	Adopt new calibration curve if orifice damaged or replace orifice unit
Sampler (in operation)	% deviation = 100 (Qo-Qc)/Qc within 5% Q_o = observed flow rate Q_c = flow rate from calibration curve	Calibration orifice unit on receipt and after major maintenance on sampler	Rerun points for which % deviation exceeds $\pm$ 5% until acceptance limits attained

Chapter 15
Quality Assurance and Quality Control

1 Need for Quality Assurance

Many studies have shown that analytical results are often subject to serious errors, particularly at the low concentrations encountered in environmental samples. In fact, the errors may be so large that the validity of actions taken regarding management of environment may become questionable,

Nutrients, N and P, in very small concentrations can cause eutrophication of water bodies. An analytical quality control (AQC) exercise conducted by United States Environmental Protection Agency (US-EPA) showed a wide variation in results when identical samples were analysed in 22 laboratories:

Nutrient	Concentration, mg/L	Range of results, mg/L
Ammonia	0.26	0.09 - 0.39
	1.71	1.44-2.46
Nitrate	0.19	0.08 - 0.41
Total phosphorus	0.882	0.642 - 1.407

It is seen that the range of values reported are significantly large, $\pm$50% for ammonia and $\pm$100% for nitrates, compared to the actual concentrations, Therefore, the need for nutrient control programme and its results become difficult to assess.

Many laboratories analyzing water quality report total dissolved salts (TDS) calculated from the electrical conductivity (EC) value:

$$TDS, mg/L = A \times EC, \mu S/cm$$

where A is a constant ranging between 0.55 and 0.9 depending on the ionic composition of salts dissolved in the water.

An inter-laboratory AQC exercise conducted by Central Pollution Control Board (CPCB) showed that for measurement of EC of a standard solution, out of 44 participating, laboratories only 34% reported values in the acceptable range. Figure 1.

Thus, the reliability of iso-concentrations of TDS in groundwaters, drawn based on data of several laboratories may become questionable on two counts; use of an arbitrary value for the constant A and variation in inter-laboratory measurements.
These examples amply demonstrate the need for quality assurance (QA) programmes.

2 Quality assurance programme

For any QA programme it is important to explicitly state, in detail, the quality requirement of the product, in our case the analytical data, its precision and accuracy.

The QA programme for a laboratory or a group of laboratories should contain a set of operating principles and procedures, written down and agreed upon by the organisation, delineating specific functions and responsibilities of each person involved and the chain of command, which would produce analytical data of required accuracy. It is necessary that the top management agrees to the 'quality policy'; it requires financial commitment. The next step is that all levels in the organization accept this concept, the laboratory supervisor, who is responsible to the data user, the analyst and the field staff.

For effectiveness, QA requires continuing evaluation of the programme and audits. This may done by an independent group within the organization. The checking of work should be done on a regular basis, not to reward or reprimand, but to correct mistakes. It should be based on notion that everybody makes mistakes and one can learn from one's mistakes. Striving for quality is not equal to striving for perfection. The analytical data has a good quality when it is fit for use.

Various aspects of a QA programme are noted below.

Sample control and documentation

Procedures regarding sample collection, labelling, preservation, transport, preparation of its derivatives, where required, and the chain-of-custody.

Mistakes in sampling will have an influence on the monitoring results. There is no possibility to reproduce a sample, there is only a probability based on expert judgement, that there is little or no change since the erroneous sample was taken. Because of the importance of proper sampling, slJecial attention should be paid to the motivation of the staff involved in sampling. Proper training and facilities can help, but also feed back of monitoring results to the field staff may provide attachment to the programme.

Standard analytical procedures

Procedures giving detailed analytical method for the analysis of each parameter giving results of acceptable accuracy should be clearly defined.

Analyst qualifications

Qualifications and training requirements of the analysts must be specified. The number of repetitive analyses required to obtain result of acceptable accuracy also depends on the experience of the analyst.

Equipment maintenance

For each instrument, a strict preventive maintenance programme should be followed. It will reduce instrument malfunctions, maintain calibration and reduce downtime. Corrective actions to be taken in case of malfunctions should be specified.

Calibration procedures

In analyses where an instrument has to be calibrated, the procedure for preparing a standard curve must be specified, e.g., the minimum number of different dilutions of a standard to be used, method detection limit (MDL), range of calibration, verification of the standard curve during routine analyses, etc.

Analytical quality control

This includes both *within-laboratory* AQC and *inter-laboratory AQC.*
Under the within-laboratory programme studies may include: recovery of known additions to evaluate matrix effect and suitability of analytical method; analysis of reagent blanks to monitor purity of chemicals and reagent water; analysis of sample blanks to evaluate sample preservation, storage and transportation; analysis of duplicates to asses method precision; and analysis of individual samples or sets of samples (to obtain mean values) from same control standard to check random error. *Inter-laboratory* programmes are designed to evaluate laboratory bias and requires participation of a reference laboratory.

AQC exercise are not one time exercises but rather internal mechanisms for checking performance and protecting laboratory work from errors that may creep in. Laboratories who accept these control checks will find that this results in only about 5 percent extra work.

In Summary:

AQC is:

- an internal mechanism for checking your own performance

- protecting yourself from a dozen of errors that may creep into analytical work
- to avoid human errors in routine work
- practiced by responsible chemists
- not useless work
- common practice in certified laboratories

AQC is NOT:

- much work
- to be carried out for each and every routine sample.
- checking and reporting the quality of your work
- a one time exercise to be forgotten soon

Data reduction, validation and reporting

Data obtained from analytical procedures, where required, must be corrected for sample size, extraction efficiency, instrument efficiency, and background value. The correction factors as well as validation procedures should be specified. Results should be reported in standard units. A prescribed method should be used for reporting results below MOL.

An important aspect of reporting the results is use of correct number of significant figures. In order to decide the number of significant digits the uncertainty associated with the reading(s) in the procedure should be known. Knowledge of standard deviation will help in rounding off the figures that are not significant. Procedures regarding rounding off must be followed.

3 Shewhart control charts

If a set of analytical results is obtained for a control sample under conditions of routine analysis, some variation of the observed values will be evident. The information is said to be statistically uniform and the analytical procedure is said to be under statistical control if this variation arises solely from random variability. The function of a control chart is to identify any deviation from the state of statistical control.

Shewhart control chart is most widely used form of control charts. In its simplest form, results of individual measurements made on a control sample are plotted on a chart in a time series. The control sample is analysed in the same way as the routine samples at fixed time intervals, once or twice every week, or after 20 to 50 routine samples. .

Assuming the results for the control sample follow the Normal frequency distribution, it would be expected that only 0.3% of results would fall outside lines drawn at 3 standard deviations above and below the mean value called upper and lower control limits, UCL and LCL, respectively. Individual results would be

expected to fall outside these limits so seldom (3 out of 1000 results), that such an event would justify the assumption that the analytical procedure was no longer in statistical control, Le., a real change in accuracy has occurred.

Two lines are inserted on the chart at 2 standard deviations above and below the mean value called upper and lower warning limits, UWL and LWL, respectively. If the method is under control, approximately 4.5% of results may be expected to fall outside these lines.

This type of chart provides a check on both random and systematic error gauged from the spread of results and their displacement, respectively. The following acti9ns may be taken based on analysis results in comparison to the standard deviation.

Control limit: If one measurement exceeds the limits, repeat the analysis immediately. If the repeat is within the UCL and LCL, continue analyses; if it exceeds the control limits again, discontinue analyses and correct the problem.

Warning limit: If two out of three successive points exceeds the limits, analyse another sample. If the next point is within the UWL and LWL, continue analyses; if the next point exceeds the warning limits, discontinue analyses and correct the problem.

Standard deviation: If four out of five successive points exceed one standard deviation, or are in increasing or decreasing order, analyse another sample. If the next point is less than one standard deviation away from the mean, or changes the order, continue analyses; otherwise discontinue analyses and correct the problem.

Central line: If six successive points are on one side of the mean line, analyse another sample. If the next point changes the side continue the analyses; otherwise discontinue analyses and correct the problem.

Figure 2 to Figure 4 illustrate some of the cases of loss of statistical control for analysis of individual samples based on the above criteria.

4 Discussion of results

Precision

The most important parameter to evaluate in the results is the precision. The statistical term to evaluate precision is standard deviation. The numerical value of the standard deviation depends on the average concentration Numerical values of standard deviations of low concentration solutions are usually smaller than those of solutions with higher concentrations. Therefore the coefficient of variation, should be used to evaluate precision. This is particularly useful when comparing results of analysis for samples having different concentrations.

For example, for results of two sets of analyses, performed on two different samples, if the mean values are 160 and 10 mg/L and standard deviations are 8 and 1.5 mg/L, respectively, comparison of standard deviation would indicate lower precision for the first

set of observations (standard deviation 8 mg/L), while the CV values work out to be 5 (8/160 x 100) and 15 (1.5/10 x 100) percents respectively, indicating a lower precision for the second set of observations.

Before evaluating the results one should answer the question 'what is the desired precision for an analysis?'. In fact this question should be answered by the so called 'data users'. The use of the data determines the required precision, e.g. detection of trends may require more precise results in order to actually detect small changes with respect to time.

As a minimum goal for precision, however, the precision that can be obtained by correctly and adequately following the prescribed method should be adopted.

Calculating revised limits when continuing the exercise

Warning and control limits should be recalculated periodically. Especially when new techniques are introduced, the precision improves when experience is gained with the technique. A good time for recalculating the control and warning limits is at the time when the control chart is full and a new graph has to be created anyway. At this point, use the 20 most recent data on the old chart for construction of LCL, LWL, average, UWL and UCL.

Errors that cannot be detected by within-laboratory AQC

The within-laboratory AQC exercise focuses mainly on precision. A laboratory on its own cannot detect many sources of bias. If the analytical balance in a laboratory always reads 10% too much all solution prepared will have a 10% higher concentration: For example, in the hardness determination by titrimetric procedure the standard $CaCO_3$ solution, the EDT A titrant and also the control sample containing $CaCO_3$ will all have 10% higher concentration and therefore the error will not be detected. This error can only be detected by analysing a sample prepared by a laboratory with a correctly functioning balance. The current laboratory will underestimate the concentration of such a inter-laboratory sample also by 10% because their EDTA titrant would be' 10% too strong'.

In some cases freshly introduced bias may be detected. For example, if the measurements consistently fall on one side of the previously calculated mean, it indicates a freshly introduced bias. An inter-laboratory AQC exercise should be conducted for detecting bias or accuracy for analysis.

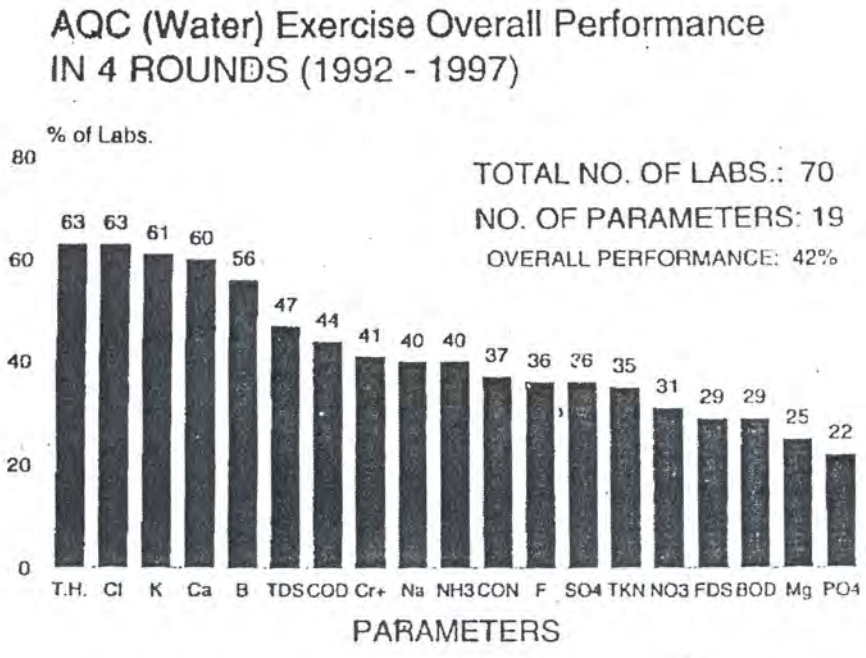


FIGURE 1 OVERALL PERFORMANCE OF LABORATORIES IN INTER-LABORATORY AQC CONDUCTED BY CPCB, INDIA.

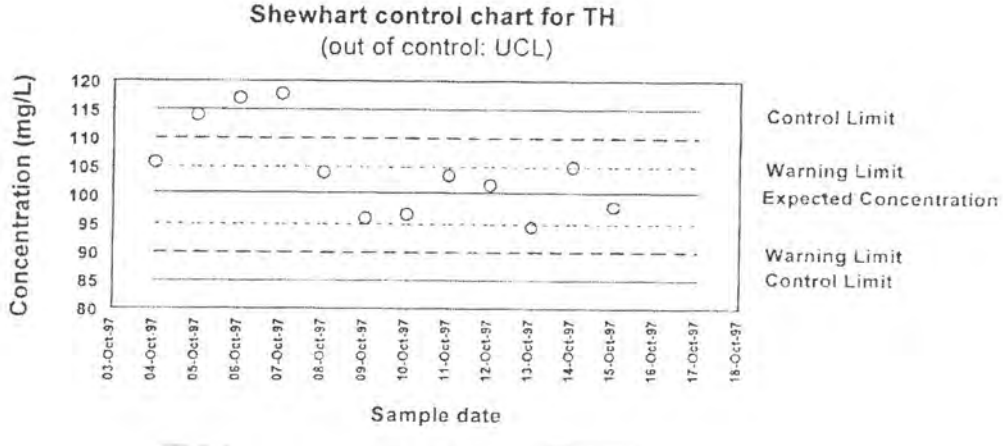


FIGURE 2 EXAMPLE OF LOSS OF STATISTICAL CONTROL BY THE CONTROL LIMIT CRITERION.

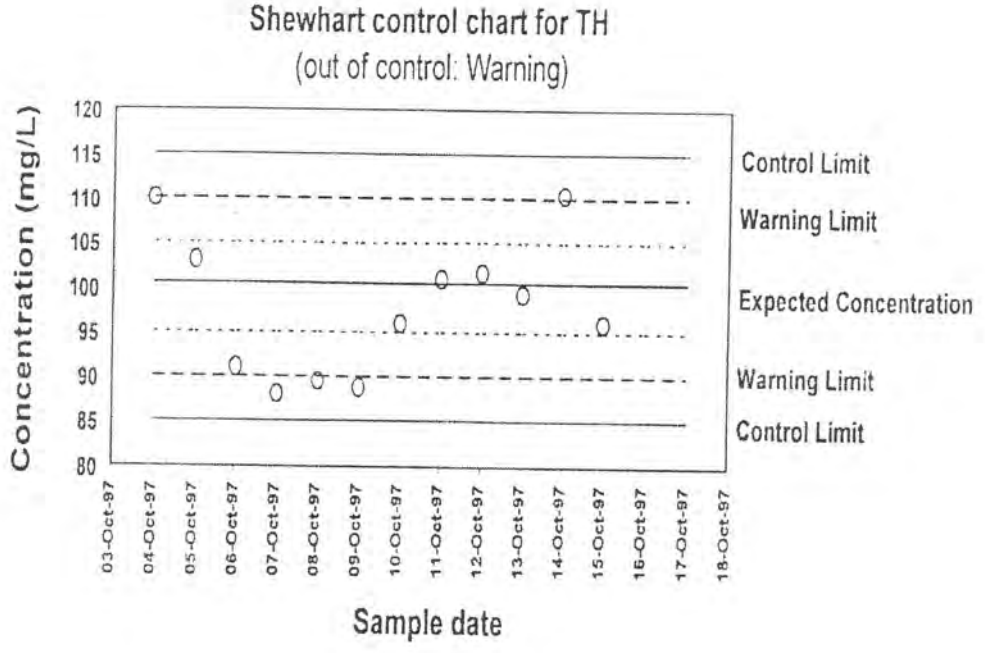


FIGURE 3 EXAMPLE OF LOSS OF STATISTICAL CONTROL BY THE WARNING LIMIT CRITERION.

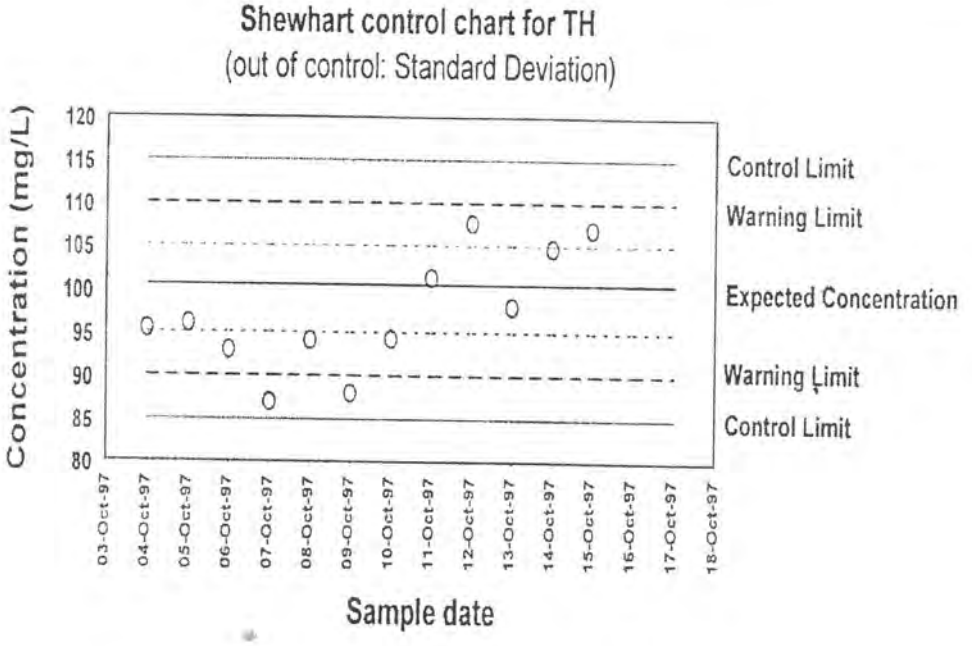


FIGURE 4 EXAMPLE OF LOSS OF STATISTICAL CONTROL BY THE STANDARD DEVIATION LIMIT CRITERION.

Chapter 16
Good laboratory Practice

A number of laboratory operations and precautions related to analysis of water quality parameters must be routinely performed in a laboratory to obtain reliable information. These practices are termed good laboratory practices. Some analyses that may measure extremely small level of contaminants or use advanced level instrumentation would require special precautions. Practices that are to be followed routinely and are basic in nature to all determinations are described here.

1. Chemicals and reagents

Purity of reagents has an important bearing upon the accuracy that can be attained in an analysis. Commercially available chemicals are routinely classified as, technical grade, laboratory or analytical reagent grade, primary-standard grade and special purpose reagents.

Technical grade reagents in general are not used in a laboratory. Where bulk quantities may be required or when purity is not of major concern, such as preparation of chromic acid cleaning solution, technical grade reagents may be used.

Routine analyses in a water testing laboratory may be performed mostly using laboratory or analytical reagent grade chemicals. Where primary standards are to be made, primary standard grade reagent should be used.

Special purpose reagents are required for analyses in which micro-level contaminants are measured, such as atomic absorption spectroscopy and gas chromatography.

The following rules should always be followed while handling reagents and chemicals:

1. As far as possible, use the smallest packing of chemical that would supply the desired quantity.
2. Replace the cap or stopper of the bottle immediately after taking out your requirement.
3. Stoppers of reagent bottles should never be placed on the desktop.
4. Do not insert spatulas or pipettes in reagent bottles. Takes out a slightly excess amount in another container from where use the required quantity.
5. Never return any excess chemical or reagent to a bottle.
6. Some reagents require special storage conditions, such as dark colour bottles for light sensitive chemicals or low temperature for solvents and reagents subject to microbial degradation.
7. Do not use a reagent after the recommended shelf life.
8. Dry solid chemicals for making solutions, in a suitable container, as directed in the standard analytical procedure for the determination.

2 Cleaning of glassware

Volume calibrations are blazed on clean volumetric equipment. Cleanliness of volumetric glassware is therefore particularly important if callibration is to have any meaning. Only clean glass surfaces will support a uniform film of liquid; the presence of dirt or oil will tend to cause breaks in this film. The existence of breaks is a certain indication of an unclean surface. A brief soaking in warm detergent is usually sufficient to remove the grease and dirt responsible for causing the water breaks.

Where detergent is not effective, rinse glassware, except that used for chromium and manganese analysis, with a cleaning mixture made by adding 1L of conc. H_2SO_4 slowly with stirring, to 35 mL saturated sodium dichromate solution. Rinse with other concentrated acids to remove inorganic matter.

Use detergents or conc. HCl for cleaning hard rubber and plastic bottles.

After the glassware and bottles have been cleaned, rinse thoroughly with reagent water.

3 Distilled or reagent water

Laboratories are provided with stainless steel water distillation stills. Distilled water obtained from such stills is of adequate purity for making reagent solutions for routine analyses carried out in water testing laboratories and cleaning of glassware. However, in case of analyses for micro-level contaminants better quality distilled water may be needed.

Distilled water may be classified on the basis of its electrical conductivity (EC) as follows:

Type	EC, µmho/cm
I	< 0.1
II	< 1
III	< 10

Ion exchange columns and double distillation, all glass water stills are used to obtain type I and II distilled water, respectively.

In the operation of water stills care should be taken to run the condenser cooling water whenever the still is in use. All stills are prone to scaling and accumulation of precipitated salts, which if not attended to results in carry over of salts in distillate and will ultimately lead to overheating and damage the heating elements. The scales should be periodically removed by dissolving in dilute solution of HCl.

In the case of ion exchange columns a record should be kept of the volume of the product water and. its EC value. The resin should be regenerated as per the supplier's

instruction when the EC value exceeds the limit.

4 Measurement of mass or weighing

Accurately measuring mass of substances is a fundamental requirement for almost all types of analyses. In the laboratory the mass is determined by comparing the weight of an object with the weight of a set of standard masses using a balance. Because acceleration due to gravity affects both the known and unknown to the same extent, equality of weight indicates equality of mass. The terminological distinction between mass and weight is, therefore, seldom made.
Analytical balances, with an accuracy of $\pm$0.1 mg, are commonly used to determine the weight. For analyses for micro-level contaminants balances with a precision of :to.01 may be used. It is of paramount importance that balances are used and maintained with great care. To avoid damage or minimize wear on the balance and obtain accurate weights adhere to the following rules:

1. Be certain that the arresting mechanism of the beam is engaged whenever the loading on the balance is being changed and when the balance is not in use.
2. Centre the load on the pan insofar as possible.
3. Protect the balance from corrosion. Only non-reactive glass, plastic or metal objects should be placed directly on the pan. In case of volatile or corrosive substances, take special precautions of sealing it in a weighed glass ampoule.
4. Do not attempt to adjust or repair the balance if you are not trained to do so.
5. Keep the balance and its case scrupulously clean. A camel's hair brush is useful for cleaning any spilled material or dust.
6. Do not weigh an object that has been heated until it has returned to the room temperature.
7. Do not touch a dried object with bare hands: use tongs to prevent the uptake of moisture.
8. Always place the balance on a vibration free platform.

The drying of a chemical or a container to constant weight is the process in which the object is first heated at an appropriate temperature, ordinarily for an hour or more, following which it is cooled and weighed.

Solids are conveniently dried and stored in weighing bottles of glass or plastic. Oven drying, usually at 105 to 110 °C is the commonest way of removing the absorbed moisture. The dried objects are stored in a desiccator while cooling. The base section of the desiccator contains a quantity of a chemical drying agent, such as anhydrous calcium chloride, calcium sulphate, or anhydrous magnesium perchlorate.

5 Recording of data

A laboratory notebook is needed to record measurements and observations concerning an analysis. The notebook itself should be permanently bound with a hard cover. The pages should be consecutively numbered. The first few pages should be reserved for a

table of contents which should be kept up to date.

1. All data should be directly entered into the notebook.
2. Entries should be labeled. Entries should not be crowded.
3. Each notebook page should be dated as it is used.

4. An erroneous entry should never be erased, obliterated or written over. Instead it should be crossed out with a single horizontal line and the correct entry should be located adjacent to it.
5. Pages should never be removed from the notebook. It is sufficient to draw a single line diagonally across a page that is to be disregarded.

6 Maintenance of equipment

A chemical laboratory is provided with a variety of equipment ranging from simple heating devices to more complicated instrumentation. Their purpose, maintenance and care aspects are discussed in other modules. It is a good practice to keep a separate logbook for each major equipment where details of their use, maintenance schedule, breakdowns and repairs, accessories, supply of consumables, etc., are carefully entered. Such a record will help in properly maintaining the instrument and planning for future.

7 Sample collection and preservation

All laboratories interact with field staff who carries out sampling, conduct site analyses and transports samples. The staff of the chemical laboratory must advise the field staff regarding procedures for site analyses and method of sample collection. The laboratory staff should also specify preservation technique of samples for different analyses to be carried out in the laboratory and supply reagents required for preservation. The laboratory staff should make it a practice to periodically visit the sampling sites, observe the procedures being carried out and advise as necessary.

Sampling procedures, different types of samplers, preservation, etc., are--described in the modules on surface and groundwater sampling procedures.

8 Laboratory safety

All laboratory employees must make every effort to adhere to certain basic safety rules to protect themselves and their fellow workers. The sources of hazard in a laboratory are corrosive and poisonous chemicals, broken glass, explosion, fire and electrical shock. Some common rules are given below. In case a health and safety programme has been developed for your laboratory, you should always follow it.

1. Learn the locations of eye fountain, emergency shower, fire blanket and fire extinguisher.
2. Eye protection must be worn at all times.

3. In handling all chemicals, avoid contact with skin. In the event of such contact, immediately wash the affected area with copious amounts of water.
4. Avoid working alone in a laboratory if the procedures to be conducted are hazardous.
5. Do not drink, eat or smoke in areas where laboratory chemicals are present. Do not drink from laboratory glassware.
6. Do not store food or beverages in storage areas and refigerators that are used for laboratory operations.
7. Always use a bulb to draw chemicals in a pipette. Never use the mouth to provide suction.
8. Be extremely tentative in touching the objects that have been heated.
9. Always fire polish the ends of freshly cut glass tubing. Never attempt to force glass tubing through a hole in the stopper. Instead, make sure that both the tubing and the hole are thoroughly wet with soapy water and protect hands with towel or heavy gloves.
10. Use fume hoods where toxic or noxious gases or fumes are likely to be evolved.
11. Use care in testing for odours; use the hand to waft vapours above containers towards nose.
12. In some locations it may not be permissible to flush heavy metals or poisonous substances down the drain. In case of such restrictions, alternative arrangements are required.

9 Analytical quality control

The subject of analytical quality control is discussed in other modules in detail. Briefly, it is an internal mechanism for checking your own performance. It indicates human errors in routine laboratory work and protects procedures from errors that may creep in due to various reasons. It is practiced by all responsible chemists and is a requirement for certification of laboratories. It is strongly recommended that laboratories conduct such a programme on routine basis.

PROCEDURE FOR PREPARATION OF DISTILL WATER USING DISTILLATION APPARATUS

1. Add some glass beads or boiling chips in the clean distillation flask.
2. Take 1.5 litre tap water in the distillation flask.
3. Keep The distillation flask on the heating mantle.
4. Connect T-shaped glass tube with distillation flask.
5. Connect Condenser with T-shaped glass tube..
6. Regulate the water supply through the inlet and outlet of the Condenser.
7. Set the temperature at heating mantle at 150°C using regulator.
8. Collect the distillate (distilled water) in such a manner that it should not be exposed to atmospheric CO_2 of the ambient environment.
9. Check the Conductivity of the distillate, if the Conductivity of the distillate is more than 3μmho/cm at 25 ° C, then re-distillate the distilled water collected and test the Conductivity. In re-distillation the Conductivity need to be achieved less than 3μmho/cm.
10. Store the distilled Water in the clean glass/Polyethylene/ other suitable plastic container which do not affect the quality of the water. No air space need to be left in the Container before sealing the bottle.

Precaution:-

1. Need to be proper greased the various joints of the distillation assembly.
2. Cold water need to be circulated through the condenser and it should be stopped after one hour of stopping power supply to heating mantle.
3. Glass beads or boiling chips need to be added in the boiling water during distillation to avoid bumping and effective heat transfer.

Chapter 17
Data reporting procedures and formats

Data reporting formats for the Malé Declaration network should be further elaborated, taking into account the progress of monitoring methodologies and so on. By using the format, the Network should be able to share regional data with known quality and in common formats, to best meet the objectives of the Network, i.e. to provide useful inputs for decision-making at local, national and regional levels.

Based on the above principle, each participating country is invited to submit a report in the attached data reporting formats on monthly basis, to the extent possible with available resources. To reduce the workload during the data compilation process, the submission of the reports via electronic media, in addition to the documents, is strongly encouraged.

Monitoring components

The participating countries are expected to monitor and report the following items:

Wet deposition monitoring

Monitoring interval

- Weekly composite samples using wet only collector.
- Weekly composite samples using bulk collector. Collector must be cleaned thoroughly at the beginning of each week to ensure that there is no dry deposition in the collector from the previous week. Rinsed water need to be analyzed for the monitoring parameters.

Monitoring parameters using wet only collector

- pH, electric conductivity (EC); reporting form: Wet W No.3
- concentration of NH_4^+, Na^+, K^+, Ca^{2+} and Mg^+; Reporting form Wet W No.2
- concentrations of SO_4^{2-}, NO_3^-, Cl^-; Reporting form: Wet W No.1

Monitoring parameters using bulk collector

- pH, electric conductivity (EC); reporting form: Wet B No.3
- concentration of NH_4^+, Na^+, K^+, Ca^{2+} and Mg^+; Reporting form Wet B No.2

concentrations of SO_4^{2-}, NO_3^-, Cl^-; Reporting form: Wet B No.1

Air concentration monitoring

Monitoring sites and interval

- Gaseous samples: 1x9 hr samples + 1x14.5 hr sample [Day sample: 9 am – 6 pm; 9hrs; night sample: 6.30 pm – 9 am; 14.5 hrs]. Sampling to be done for 10 days/month between 5^{th} – 25^{th} of each month.
- Dust samples: 1x24 hr samples [9 am – 9 am next day].Sampling to be done 10 days/month between 5^{th} – 25^{th} of each month.
- Valid sample: when machine up time is >60% of sampling time

- Diffusive (passive) samplers: Monthly

Measurement parameters
- PM_{10}, NRSPM, TSPM, SO_2 and NO_x; Reporting form: Air H
- Concentration of SO2 and NO2 using passive sampler; Reporting form: Air P

Meteorological measurement

- wind direction/speed, temperature, humidity, precipitation amount and solar radiation (in accordance with the measurement frequency of the meteorological monitoring system of each country)

Monitoring site details

Site details such as land use, potential contamination sources, geographical description, climate need to be documented using the reporting form S1, S2, and S3.

Note

If the information submitted changes, the up-to-date information should be reported as soon as possible.

DATA REPORTING FOR WET ONLY COLLECTOR

Form Wet W No.1 **Results of wet deposition analysis (Anion)**

Site name : ______________________ Average funnel dian ______ (mm)

Name of Laboratory : ______________________ Name of reporter : ______________________

Sample No.	Sampling period				SO_4^{2-}	flg1	flg2	flg3	NO_3^-	flg1	flg2	flg3	Cl^-	flg1	flg2	flg3		flg1	flg2	flg3		flg1	flg2	flg3	Date of analysis	Note
	Start		End																							
	Date	Time	Date	Time	µmol/l				µmol/l				µmol/l													

DATA REPORTING FOR WET ONLY COLLECTOR

Form Wet W No.2 **Results of wet deposition analysis(Cation)**

Site name : ______________________ Average funnel dian ________ (mm)

Name of Laboratory : ______________________ Name of reporter : ______________________

Sample No.	Sampling period				NH_4^+	flg1	flg2	flg3	Na^+	flg1	flg2	flg3	K^+	flg1	flg2	flg3	Ca^{2+}	flg1	flg2	flg3	Mg^{2+}	flg1	flg2	flg3		flg1	flg2	flg3	Date of analysis	Note
	Start		End																											
	Date	Time	Date	Time	µmol/l				µmol/l				µmol/l				µmol/l				µmol/l									

DATA REPORTING FOR WET ONLY COLLECTOR

Form Wet W No.3 **Results of wet deposition analysis(EC, pH, R1 ,R2, Precipitation)**

Site name :

Average funnel diamete (mm)

Name of Laboratory :

Name of reporter :

Sample No.	Sampling period				EC	flg1	flg2	flg3	pH	flg1	flg2	flg3	R1	flg1	flg2	flg3	R2	flg1	flg2	flg3	Amount of sample	No of events	Duration of events	flg1	flg2	flg3	Amount of precipitation	flg1	flg2	flg3	Date of analysis
	Start		End																												
	Date	Time	Date	Time	mS/m																ml		hrs				mm				

flg no. comments

:

:

DATA REPORTING FOR WET BULK COLLECTOR

Form Wet B No.1 **Results of wet deposition analysis (Anion)**

Site name :

Average funnel diam (mm)

Name of Laboratory :

Name of reporter :

Sample No.	Sampling period				SO_4^{2-}	flg1	flg2	flg3	NO_3^-	flg1	flg2	flg3	Cl^-	flg1	flg2	flg3		flg1	flg2	flg3		flg1	flg2	flg3	Date of analysis	Note
	Start		End																							
	Date	Time	Date	Time	µmol/l				µmol/l				µmol/l													

DATA REPORTING FOR BULK COLLECTOR

Form Wet B No.2 **Results of wet deposition analysis(Cation)**

Site name : ______________________ Average funnel dian ________ (mm)

Name of Laboratory : ______________________ Name of reporter : ______________________

Sample No	Sampling period				NH_4^+	flg1	flg2	flg3	Na^+	flg1	flg2	flg3	K^+	flg1	flg2	flg3	Ca^{2+}	flg1	flg2	flg3	Mg^{2+}	flg1	flg2	flg3		flg1	flg2	flg3	Date of analysis	Note
	Start		End																											
	Date	Time	Date	Time	µmol/l				µmol/l				µmol/l				µmol/l				µmol/l									

DATA REPORTING FOR BULK COLLECTOR

Form Wet B No.3 **Results of wet deposition analysis(EC, pH, R1 ,R2, Precipitation)**

Site name :

Average funnel diamete (mm)

Name of Laboratory :

Name of reporter :

Sample No.	Sampling period				EC	flg1	flg2	flg3	pH	flg1	flg2	flg3	R1	flg1	flg2	flg3	R2	flg1	flg2	flg3	Amount of sample	flg1	flg2	flg3	Amount of precipitation	flg1	flg2	flg3	Date of analysis	Note
	Start		End																											
	Date	Time	Date	Time	mS/m																ml				mm					

Form: Air H **Results of air concentration analysis (High Volume Sampler)**

Site name:

Name of Laboratory:

Unit: $\mu g/m^3$

Sample No.	Sampling period				Manometer reading(m3/min)		Time totalizer reading(hrs)		Wt. of filter paper(gm)		Wt. of Dust Cup(gm)		Concentration ($\mu g/m^3$)			Remarks
	Start		End		Initial	Final	Initial	Final	Initial	Final	Initial	Final	PM_{10}	NRSPM	TSPM	
	Date	Time	Date	Time												

Form: Air H **Results of air concentration analysis (High Volume Sampler) cont…**

Site name:

Name of Laboratory:

Unit: $\mu g/m^3$

Sample No.	SO2				NOx				Loss of water due to evaporation (ml)		Absorbance value		Concentration ($\mu g/m^3$)		Ambient temperature		Remarks
	Rotometer reading (lpm)		Absorbing reagent (ml)		Rotometer reading (lpm)		Absorbing reagent (ml)										
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	SO2	NOx	SO2	NOx	SO2	NOx	Start	End	

Form: Air P **Results of air concentration analysis (Passive Sampler)**

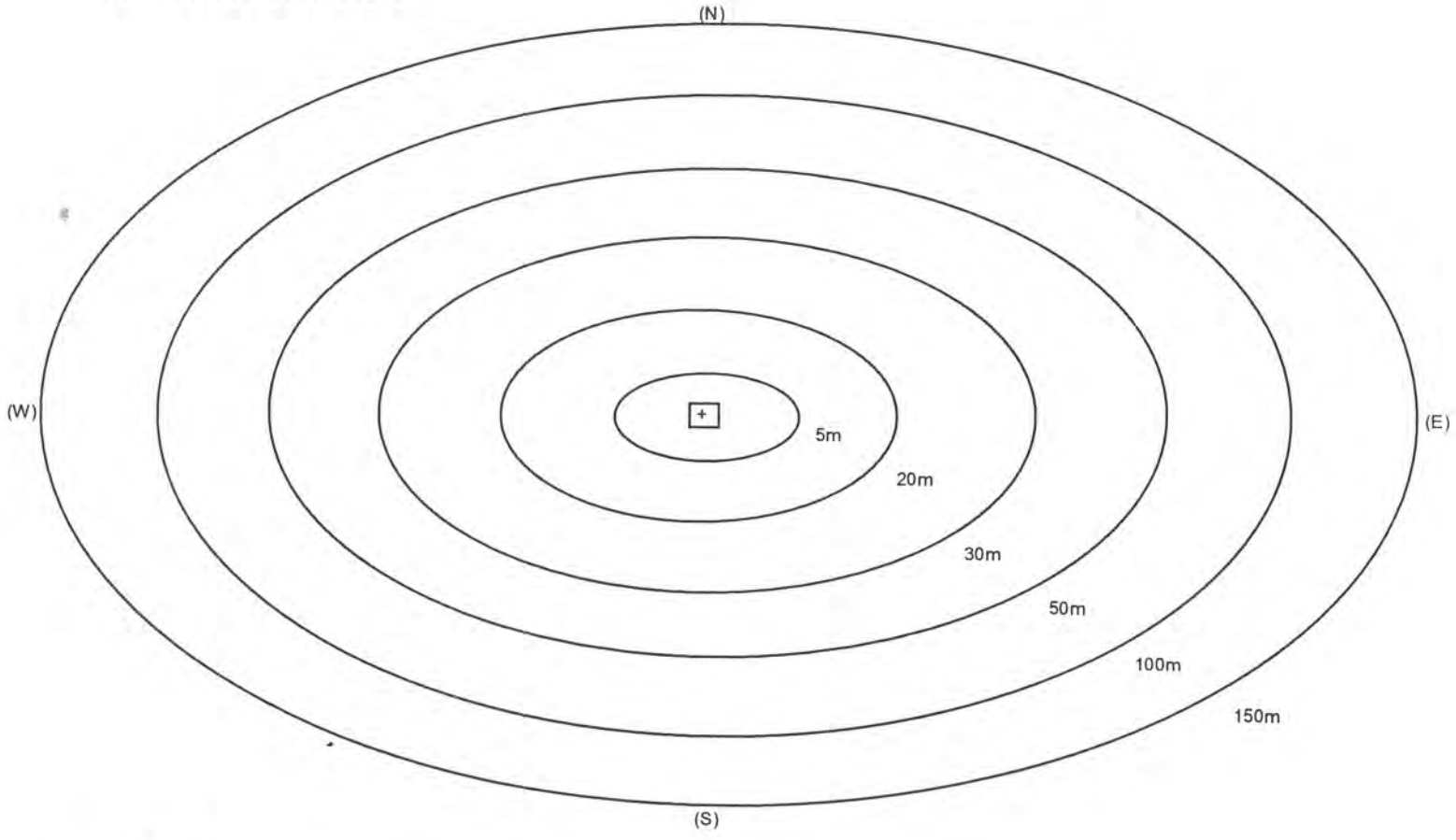
Site name: **Site Classification:**

Name of Laboratory:

Unit: $\mu g/m^3$

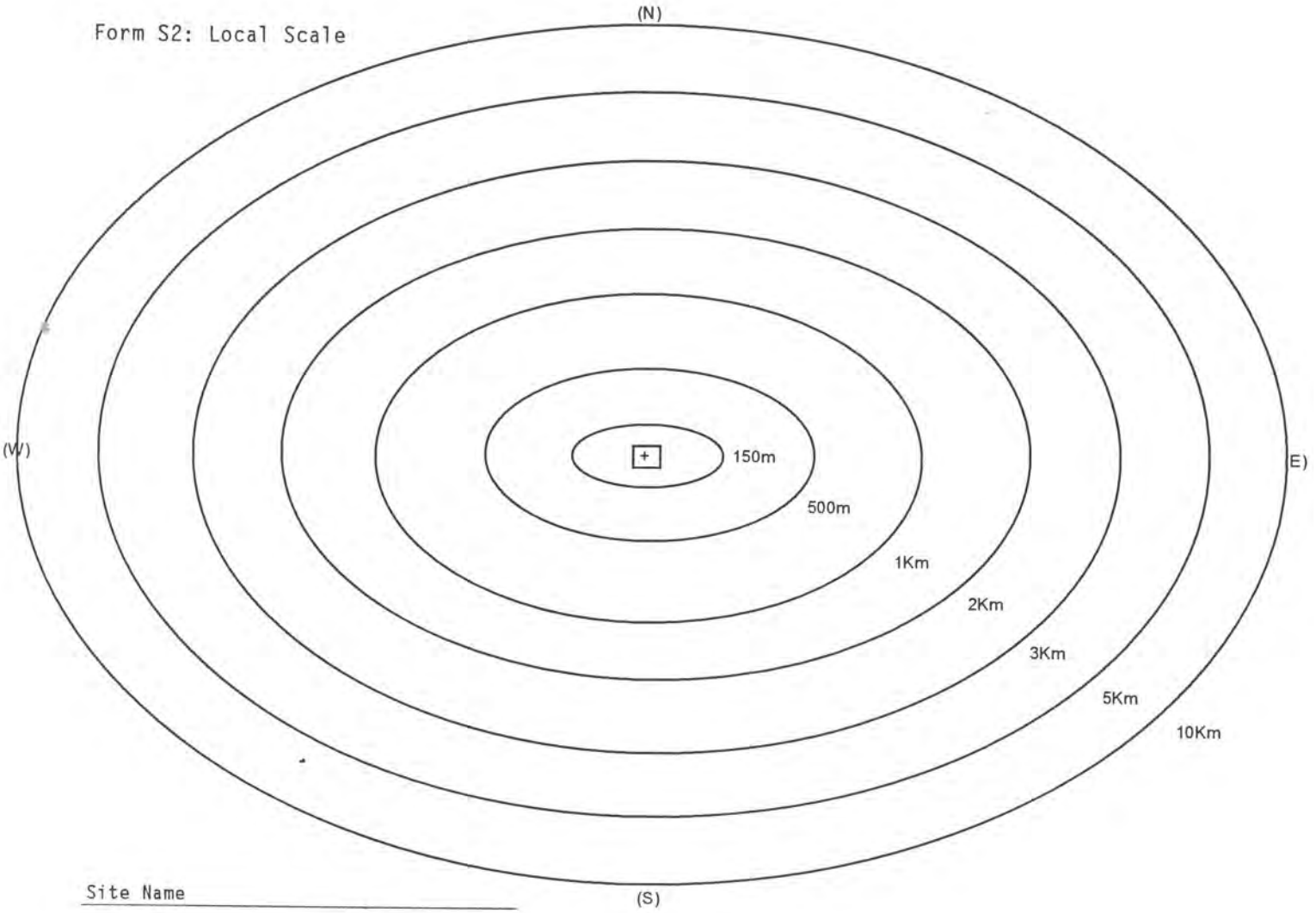
Sample No.	Sampling period				Concentration	
	Start		End		SO_2	NO2
	Date	Time	Date	Time		

Form S1 :On-site Scale



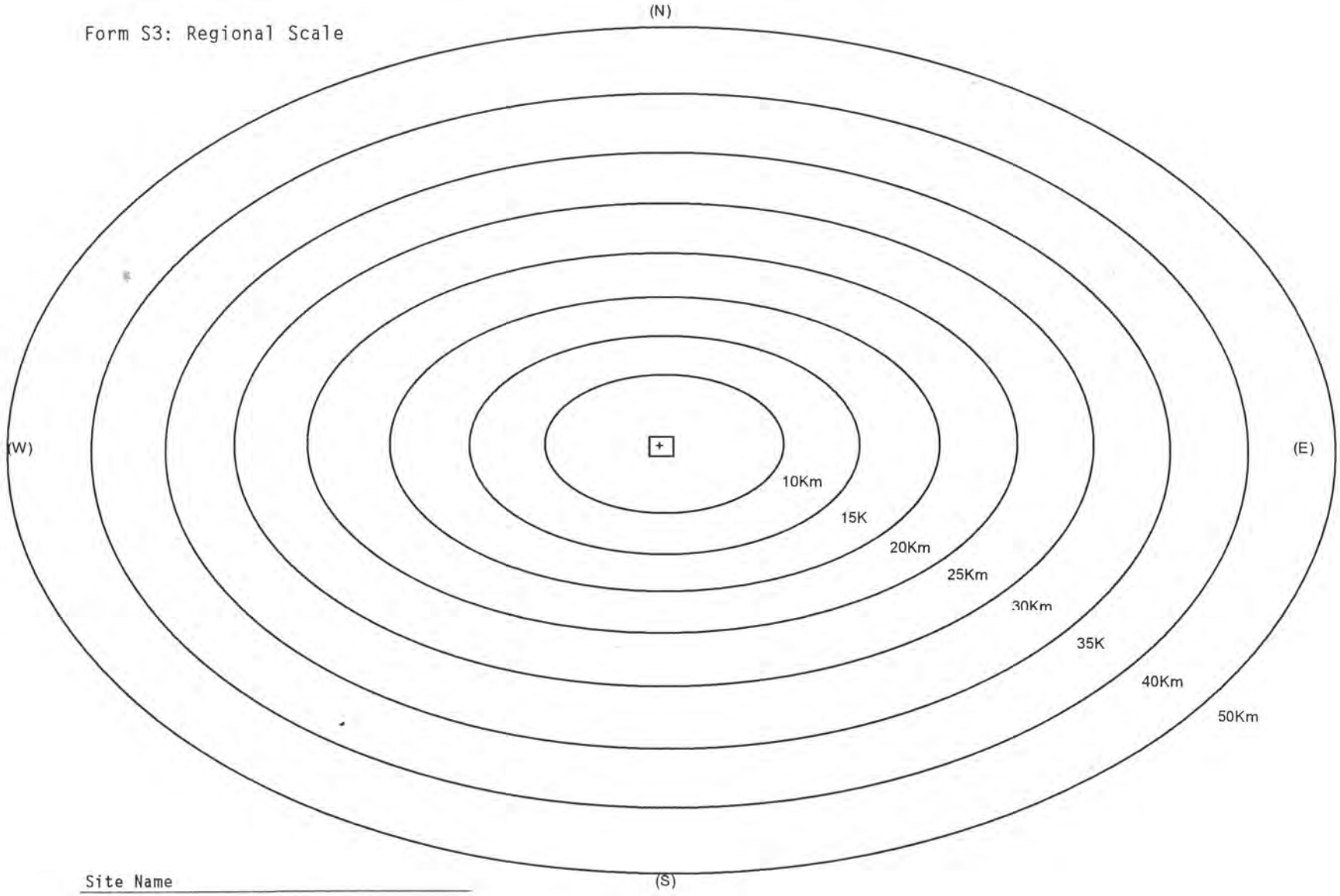
Site Name _____

Form S2: Local Scale



Site Name _____

Form S3: Regional Scale



Site Name _____

Test Methods

1.0 TITLE

Method for determination of Suspended Particulate Matter (SPM) in the Atmosphere (High Volume Method).

2.0 PURPOSE

The purpose is to lay down an uniform and reliable method for measurement of Suspended Particulate Matter (SPM) in the ambient air.

3.0 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 (40 ft^3/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 (1,2).

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

3.2 Range and Sensitivity

3.2.1 **Lower Quantifiable Limit** - For a 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 then approximately 3.5 $\mu g/m^3$. The three-sigma lower quantifiable limit depends on the filter used and may be as high as 5 $\mu g/m^3$.

3.2.2 **Upper Quantifiable Limit** - For a 24-h sample duration at 1132 L/min, this limit is in the range of 400 to 1000 $\mu g/m^3$. 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.

4.0 SCOPE

This method is applicable for determination of suspended particulate matter in the ambient air.

5.0 INTERFERENCES

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

5.2 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.

5.3 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 (4), 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 (5) or by ducting blower exhaust away from the sampler.

5.4 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 (6, 7)

5.5 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 (8). Increased mass deposits of 50% or more have been observed as RH increases to 100% (9). Twenty-four hours at a constant temperature and RH is considered adequate for sample equilibration.

5.6 **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.

5.7 Precision and Accuracy

5.7.1 Mass of the filter deposit, flow rate through the filter, and sampling time have typical precision of $\pm$ 2 mg, $\pm$5%, and $\pm$ 1 min, respectively, as determined from performance tests (10). 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 $\pm$ 13% at 10 $\mu g/m^3$ and approximately $\pm$ 5% at 100 $\mu g/m^3$. The filter deposit mass measurement precision dominates at low concentrations while the flow rate precision dominates at high concentrations.

6.0 APPARATUS

6.1 **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.

6.2 Size Selective Inlets

6.2.1 **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 (11,12). 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 (11).

6.3 Flow Controllers

6.3.1 **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.

6.4 **Laboratory Equipment**

6.4.1 **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 (4.16) and a relative humidity of 20 to 45% with ± 5% variability is recommended (4).

6.4.2 **Light Table** - A photographic slide viewing table is used for filter inspection.

6.4.3 **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.

6.4.4 **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.

6.4.5 **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.

6.4.6 **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.

6.5 Calibration and Auditing Equipment

6.5.1 **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.

6.5.2 **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.

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

6.5.4 **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 Kpa (4% of standard 101.3 kPa).

6.5.5 **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).

6.5.6 **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

6.5.7 **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 $\pm$ 0.5 mg of its designated weight. At each weighing session a balance calibration check is performed using a Class S of Class M weight.

7.0 REAGENTS

7.1 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 um DOP sampling efficiency in excess of 99%, weight losses or gains due to mechanical or chemical instability of less than a 5 $\mu g/m^3$ equivalent, and alkalinity of less than 25 micro-equivalent/g to minimize sulfur dioxide (SO_2) and nitrogen oxides (NOx) absorption (13). 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 material is perfect for all purposes.

7.1.1 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 (14,15). Blank levels for several elements of interest are high and variable (16,17). Glass fiber filters may exhibit organic carbon artifacts (18).

7.2 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.

8.0 PROCEDURE

8.1 Figure-3 presents a flow diagram of the routine operating procedure described in the following Sub-sections.

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

8.3 **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-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.

8.4 **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.

8.5 **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 $\pm$ 1.0 mg, read just them and re-weight the previous ten filters. Place each filter in its filter jacket when weighing is complete, but do not seal the jacket opening. A separate technician randomly selects four filters or ten percent of all filters in the batch (whichever is larger), re-weight them and subtracts this check-weight value from the corresponding routine weight. If, any check weight differs by more than $\pm$ 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.

8.6 Field Sampling - Tilt back the inlet and secure it according to manufacturer's instructions. Loosen the face-plate wing-nuts and remove the face place. Remove the filter from its jacket and center it on the support screen with the rough side of the filter facing upwards. Replace the face-plate and tighten the wing-nuts to secure the rubber gasket against the filter edge. Gently lower the inlet. Inertial jet and cyclonic inlets must have their seals in contact with the top of the face-plate. Look underneath the inlet just as it is coming into contact with the face-plate to assure that this contact is being made. It may be necessary to readjust the position of the filter/motor assembly in the sampler housing to obtain such a seal. Excessively windy and wet conditions should be avoided when changing samples. Pre-loading in a filter cartridge assembly, temporary removal of the sampler to a protected area, or a wind or rain shield may be used if, the sample must be changed in inclement weather. Set the timer for the desired start and stop time. Replace the chart paper in the flow recorder, if there is one, set the proper time, and mark the time and date on the chart. For a 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.

9.0 CALCULATIONS

9.1 Calculation of Volume of Air Sampled

$V = QT$

V = Volume of air sampled in m^3
Q = Average flow rate in m^3/minute
T = Total sampling time in minute

9.2 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	=	Initial weight of filter in g.
W_f	=	Final weight of filter in g.
V	=	Volume of air sampled in m^3
10^6	=	Conversion of g to μg.

10.0 REFERENCES

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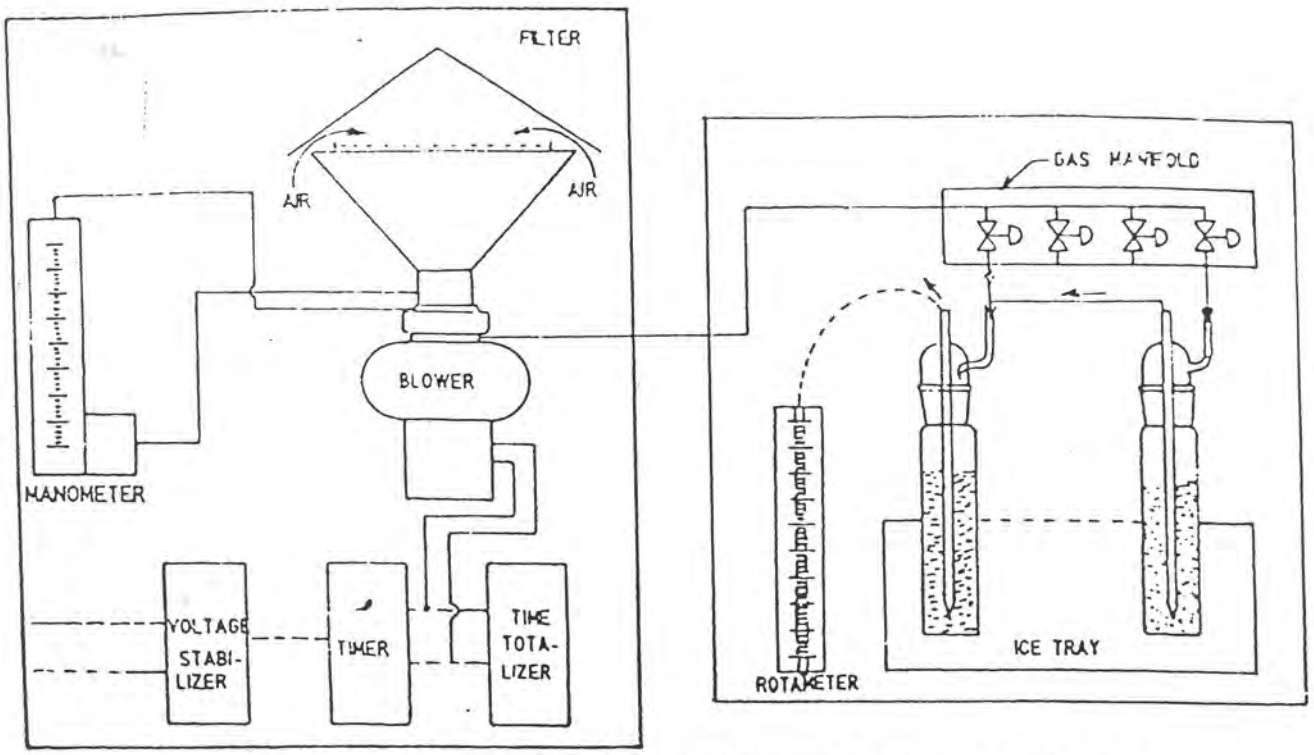

FIG. 1 SKETCH DIAGRAM OF HIGH VALUME SAMPLER

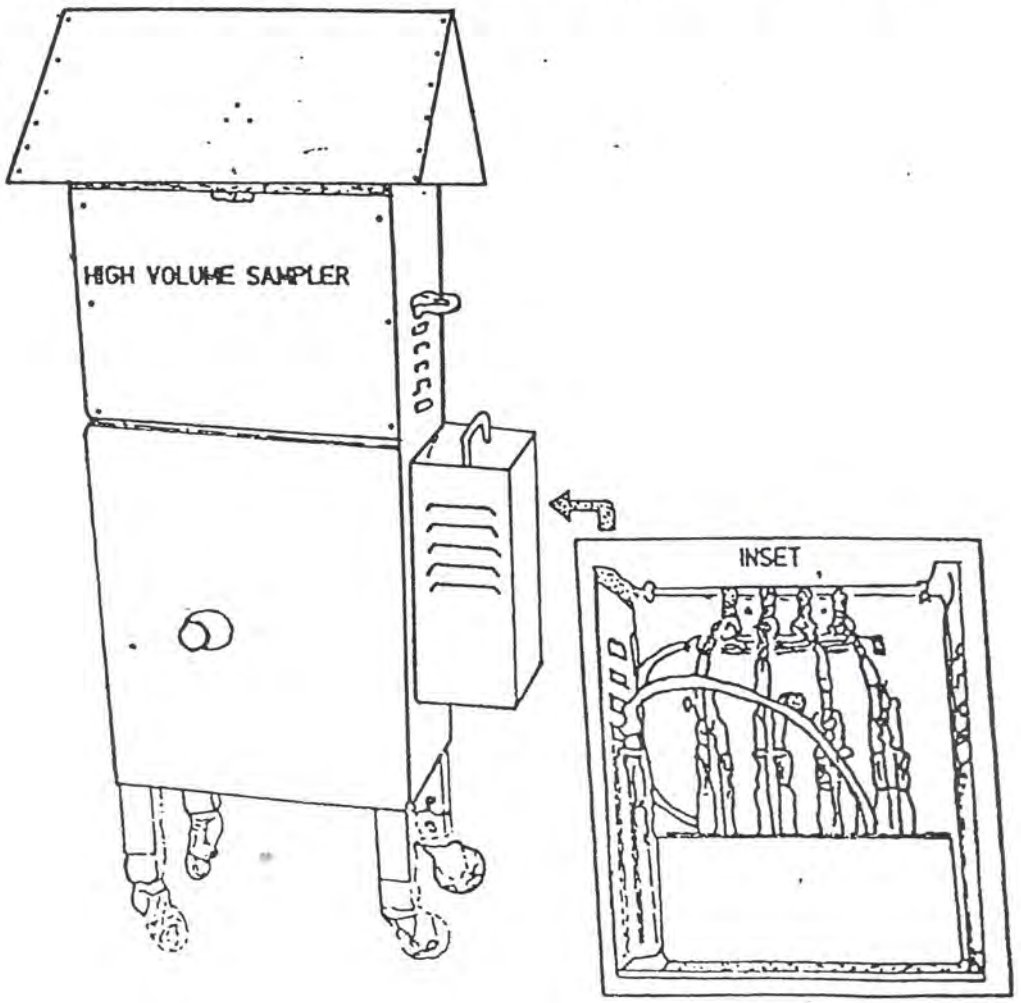

FIG. 2 HIGH VALUME SAMPLER

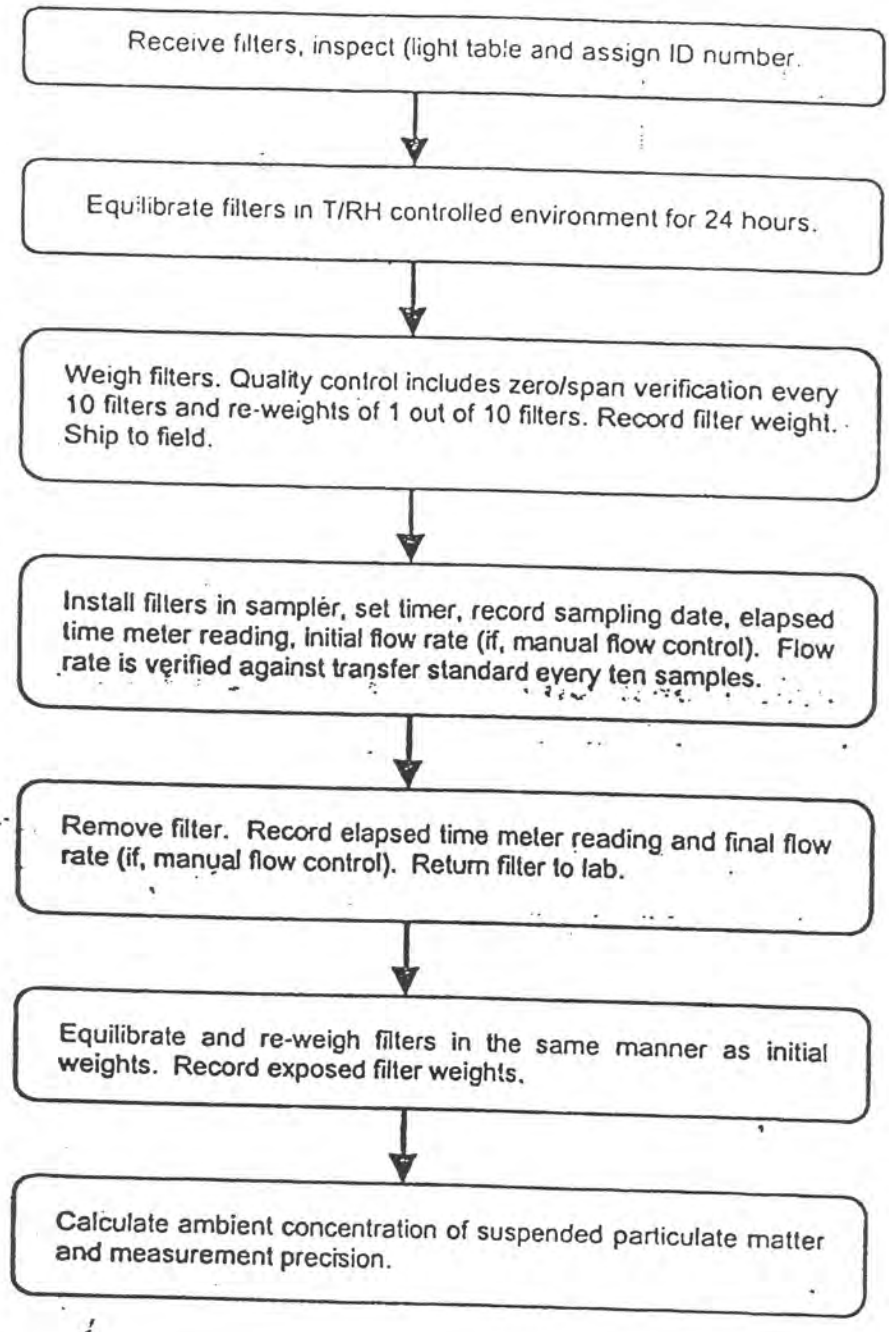

Figure 3 : Flow Diagram for Routine Hivol Operations

Appendix I

	CENTRAL LABORATORY TEST METHODS	DOC : CB/CL/TM/9/C-4
cpcb	MEASUREMENT OF RESPIRABLE SUSPENDED PARTICULATE MATTER (PM_{10}) IN AMBIENT AIR (CYCLONIC FLOW TECHNIQUE)	Issue No. : 01 Issue Date : 15.01.2001 Page No. : 1 of 9

1.0 TITLE

Method for measurement of Respirable Suspended Particulate Matter (PM_{10}) in ambient air (Cyclonic Flow Technique).

2.0 PURPOSE

The purpose is to lay down an uniform and reliable method for measurement of PM_{10} (Particulate matter less than 10 μm diameter) in ambient air.

3.0 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.

3.1 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.

3.2 Range and Sensitivity

3.2.1 Lower Quantifiable Limit - For a 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 then approximately 3.5 $\mu g/m^3$. The three-sigma lower quantifiable limit depends on the filter used and may be as high as 5 $\mu g/m^3$.

3.2.2 Upper Quantifiable Limit - For a 24-h sample duration at 1132 L/min, this limit is in the range of 400 to 1000 $\mu g/m^3$. 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.

4.0 SCOPE

This method is applicable for measurement of PM_{10} in the ambient air.

5.0 INTERFERENCES

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

5.2 Re-circulation - Re-circulation occurs when the blower exhaust, which contains and copper particles from the armature and brushes, is entrained in the samp Positive biases of 0.15 $\mu g/m^3$ have been measured, which are insignificant interferences but which may affect carbon and copper measurements. Recir be minimized by assuring a tight seal between the blower and the sampler housing ducting blower exhaust away from the sampler.

5.3 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.

5.4 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.

5.5 Shipping Losses - Particle loss during transport occurs when filters are heavil with large dry aerosols. It is more prevalent on membrane than on glass fibe Particle loss is minimized by shorter sample duration in heavily polluted enviro use of fiber as opposed to membrane filters, folding the filter prior to transpo careful shipping procedures.

5.6 Precision and Accuracy

5.6.1 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 $\mu g/m^3$ and approximately ± 5% at 100 $\mu g/m^3$. The filter deposit mass measurement precision dominates at low concentrations while the flow rate precision dominates at high concentrations.

6.0 APPARATUS

6.1 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 capable of supporting a 20.3 x 25.4 cm. glass fibre filter.

6.2 Inlet for PM_{10} Sampling

6.2.1 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 10 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.

6.3 Flow Controllers

6.3.1 **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.

6.4 Laboratory Equipment

6.4.1 **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 a relative humidity of 20 to 45% with ± 5% variability is recommended.

6.4.2 **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.

6.4.3 **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.

6.4.4 **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.

6.4.5 **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.

6.5 **Calibration and Auditing Equipment**

6.5.1 **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.

6.5.2 **Orifice Transfer Standard** - The PM_{10} 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.

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

6.5.4 **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 Kpa (4% of standard 101.3 kPa).

6.5.5 **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).

6.5.6 **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

6.5.7 **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 of Class M weight.

8.2 **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-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.

8.3 **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 equi'" ration 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.

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

8.5 Field Sampling - Tilt back the inlet and secure it according to manufacturer's instructions. Loosen the face-plate wing-nuts and remove the face plate. Remove the filter from its jacket and center it on the support screen with the rough side of the filter facing upwards. Replace the face-plate and tighten the wing-nuts to secure the rubber gasket against the filter edge. Gently lower the inlet. Inertial jet and cyclonic inlets must have their seals in contact with the top of the face-plate. Look underneath the inlet just as it is coming into contact with the face-plate to assure that this contact is being made. It may be necessary to readjust the position of the filter/motor assembly in the sampler housing to obtain such a seal. Excessively windy and wet conditions should be avoided when changing samples. Pre-loading in a filter cartridge assembly, temporary removal of the sampler to a protected area, or a wind or rain shield may be used if, the sample must be changed in inclement weather. Set the timer for the desired start and stop time. Replace the chart paper in the flow recorder, if there is one, set the proper time, and mark the time and date on the chart. For a 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.

9.0 CALCULATIONS

9.1 Calculation of Volume of Air Sampled

$V = QT$

V = Volume of air sampled in m^3

Q = Average flow rate in m^3/minute

T = Total sampling time in minute

9.2 Calculation of PM_{10} in Ambient Air

$$PM_{10} = \frac{(W_f - W_i) \times 10^6}{V}$$

Where :

PM_{10}	=	Mass concentration of particulate matter less than 10 micron diameter in $\mu g/m^3$
W_i	=	Initial weight of filter in g.
W_f	=	Final weight of filter in g.
V	=	Volume of air sampled in m^3
10^6	=	Conversion of g to μg.

10.0 REFERENCES

1. Intersociety Committee. Methods of Air Sampling and Analysis (3rd Edition) by James. P. Lodge, Sr. Editor. Lewis Publishers, Inc.

1.0 TITLE

Method for determination of Sulphur Dioxide in Air (Modified West and Gaeke)

2.0 PURPOSE

The purpose is to lay down an uniform and reliable method for determination of sulphur dioxide (SO_2) in ambient air.

3.0 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 (5, 6). 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 (7). 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 measure 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 absorbance unit. This corresponds to 0.8-27 µg 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 µg based on twice the standard deviation, which represent a concentration of 25 $\mu g/m^3$ in an air sample of 30 litres.

4.0 SCOPE

This method is applicable for the measurement of concentration of sulphur dioxide present in ambient air.

5.0 INTERFERENCES

The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulphamic acid (1, 2, 3). Ozone is made to decompose by allowing the solution to stand for some time prior to analysis (4). The interference of trace metals may be eliminated by the addition of ethylenediamine tetra acetic acid (EDTA) to the absorbing solution prior to sampling (2, 4). 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.

6.0 APPARATUS

6.1 Sampling

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

6.1.2 Polypropylene Two-Port Tube Closures

6.1.3 Glass Impingers - Tubing, 6 cm OD 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.

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

6.1.5 Pump - Capable of maintaining an air pressure differential greater than 0.7 atm at the desired flow rate.

6.1.6 Air Flowmeter or Critical Orifice - A calibrated rotameter 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 about 0.2 litre/minute. Use a membrane filter to protect the orifice (Figure 2).

6.2 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 :

$$A = 2 - \log_{10} T$$

7.0 REAGENTS

7.1 Sampling

7.1.1 **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.

7.1.2 **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(8). The absorbing reagent is normally stable for six months. If, a precipitate forms, discard the reagent after recovering the mercury.

7.2 Analysis

7.2.1 **Sulphamic Acid (0.6%)** - Dissolve 0.6 g sulphamic acid in 100 ml distilled water. Prepare fresh daily.

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

7.2.3 **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.

7.2.4 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.

7.2.5 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.

7.2.6 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.

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

7.2.7 **Standardized Sulphite Solution for Preparation of Working Sulphite-TCM Solution** - Dissolve 0.30 g sodium metabisulphite ($Na_2S_2O_5$) or 0.40 g sodium sulphite (Na_2SO_3) in 500 ml of recently boiled, cooled, distilled water. Sulphite solution is unstable; it is, therefore, important to use water of the highest purity to minimize this instability. This solution contains the equivalent of 320-400 µg/ml of SO_2. 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 to react for 5 minutes. Prepare the working sulphite-TCM solution (section 7.2.9) at the same time iodine solution is added to the flasks. By means of a burette containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml starch solution and continue the titration until the blue color disappears.

7.2.9 **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.

7.2.10 Purified Pararosaniline Stock Solution (0.2% Nominal)

7.2.10.1 **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, section 8.5.2 should have a slope of 0.030 $\pm$ 0.002 absorbance unit/μg SO_2 at this path length when the dye is pure and the sulphite solution is properly standardized.

7.2.10.2 **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).

7.2.10.3 **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.

8.0 PROCEDURE

8.1 Sampling and Analysis

8.1.1 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.

8.1.2 **30 Minutes, 1 Hour and 4 Hours Sampling** - Insert a midget impinger into the sampling system (Figure 1). 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 1, or a critical orifice, as shown in Figure 2, 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, see section 10.1 during hot weather, sampling is not recommended unless it is possible to refrigerate the samples as taken.

8.1.3 **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; see section 10.1. During hot weather, sampling is not recommended unless it is possible to refrigerate the samples as taken.

8.1.4 **Sample Preparation** - After collection, if a precipitate is observed in the sample, remove it by centrifugation.

8.1.5 **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.

8.1.6 24 Hours Sample - Make-up the entire sample to 50 ml with absorbing solu Measure 5 ml of the sample into a 25 ml volumetric flask by pipette for che analysis. Bring volume to 10 ml with absorbing reagent. Delay analysis for 20 mi to allow any ozone to decompose.

8.2 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 (2).

8.3 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 either sample, control solution, or reagent blank, add 1 ml 0.6% sulphamic acid and allow to react 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, Ao, 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 (section 8.5.2). If, the reagent blank differs by more than 0.03 absorbance unit that found in the calibration curve, prepare a new curve.

8.4 Absorbance Range

If, the absorbance of the sample solution lies between 1.0 and 2.0, the sample is diluted 1:1 with a portion of the reagent blank and read within a few minutes. Samples 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.

8.5 Calibration and Efficiencies

8.5.1 Flowmeter and Hypodermic Needle - Calibrate flowmeter and hypodermic needle (9) against a calibrated wet test meter.

8.5.2 Calibration Curve - Procedure with Sulphite Solution - Measure by pipette graduated amounts of the working sulphite-TCM solution (Section 7.2.9) (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 as described in section 8.3. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within $\pm$ 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 (section 7.2.9) in micrograms sulphur dioxide per milliliter times the milliliter of sulphite solution added ($\mu g\ SO_2 = \mu g/ml/SO_2 \times ml$ added). A linear relationship should be obtained, and the Y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal, and denote as B, the calibration factor. See section 7.2.10.1 for specifications on the slope of the calibration curve. This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations is recommended to ensure the reliability of this factor.

8.5.3 Sampling Efficiency - Collection efficiency is generally above 98%; efficiency may fall off, however, at concentrations below 25 $\mu g/m^3$ (13, 14).

9.0 CALCULATION

9.1 Normality of Thiosulfate Solution (Section 7.2.6)

The normality of this solution, N, is calculated as follows :

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

Where :

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

9.2 Concentration of Sulphite Solution

The amount of sulphur dioxide per milliliter in the standard solution, is calcula follows :

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

Where :

C - SO_2 concentration in µg/ml
V_1 - Volume of thiosulfate for blank, ml
V_2 - Volume of thiosulfate for sample, ml
N - Normality of thiosulfate
K - 32000 (Milliequivalent weight SO_2/µg)
V - Volume of standard sulphite solution, ml

9.3 Conversion of Volume

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

$$V_r = V \times \frac{P}{760} \times \frac{298}{t + 273}$$

Where :

V_r - Volume of air at 25°C and 760 mm Hg, litres
V - Volume of air sampled, litres
P - Barometric pressure, mm Hg
t - Temperature of air sampled, °C

9.4 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 :

$$C = \frac{(A - A_o)(10^3)(B)}{V_r} \times D$$

Where :

A - 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, litres
B - Calibration factor, µg/absorbance unit
D - Dilution factor

9.5 The Concentration of SO_2 in µg/m^3 in the sample is calculated as follows:

$$C\ (SO_2\ \mu g/m^3) = \frac{(A - Ao) \times 10^3 \times B}{V}$$

Where :

A - Sample absorbance
Ao - Reagent blank absorbance
10^3 - Conversion litres to cubic meters
B - Calibration factor, µg/absorbance
V - Volume of air sampled in liters

9.6 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 :

$$ppm\ SO_2 = \mu g\ SO_2/m^3 \times 3.82 \times 10^{-4}$$

9.7 Precision and Accuracy

Relative standard deviation at the 95% level in 4.6% for the analytical procedure using standard samples (3).

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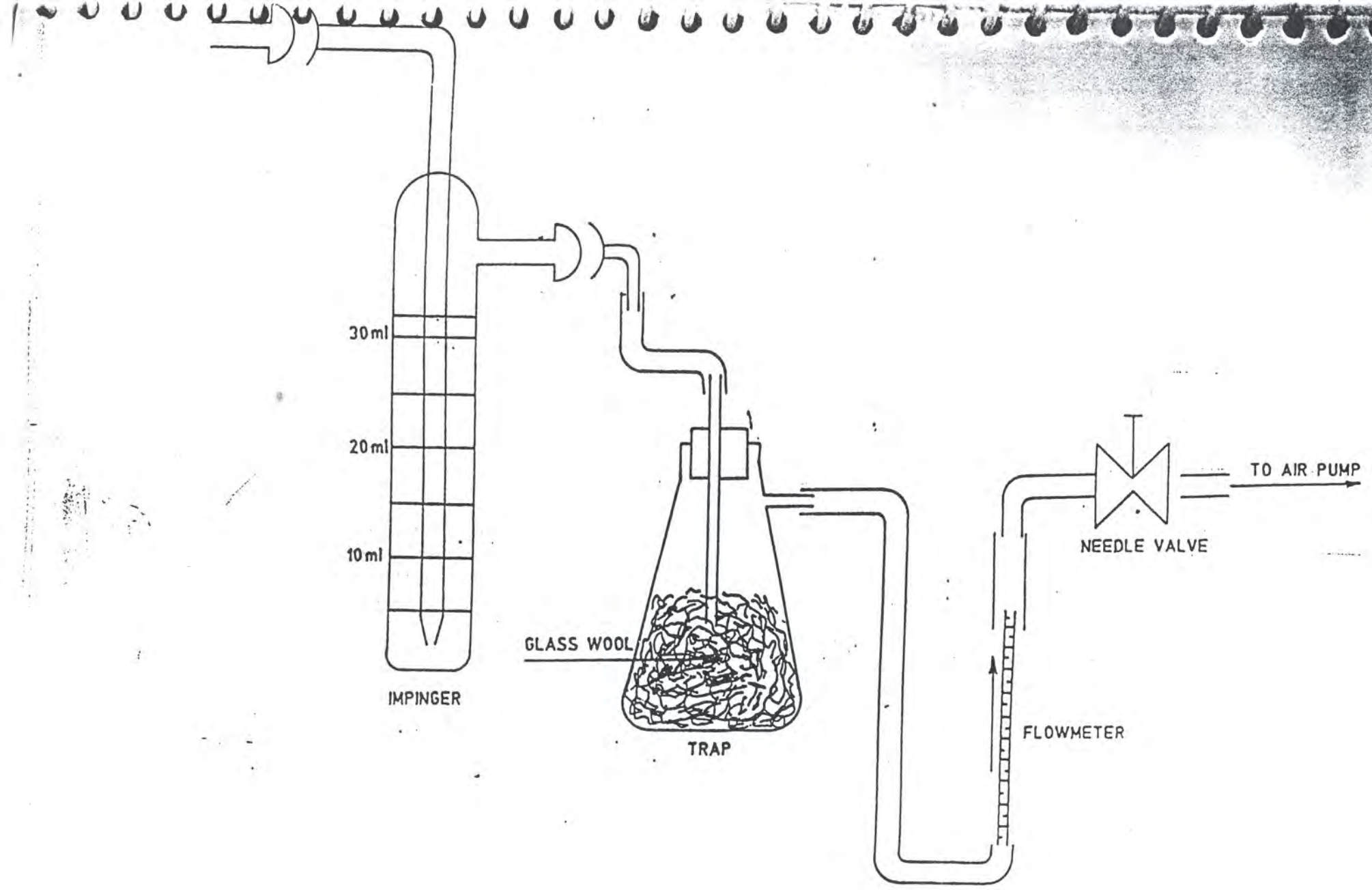

FIG. 1.0 SO2 SAMPLING TRAIN

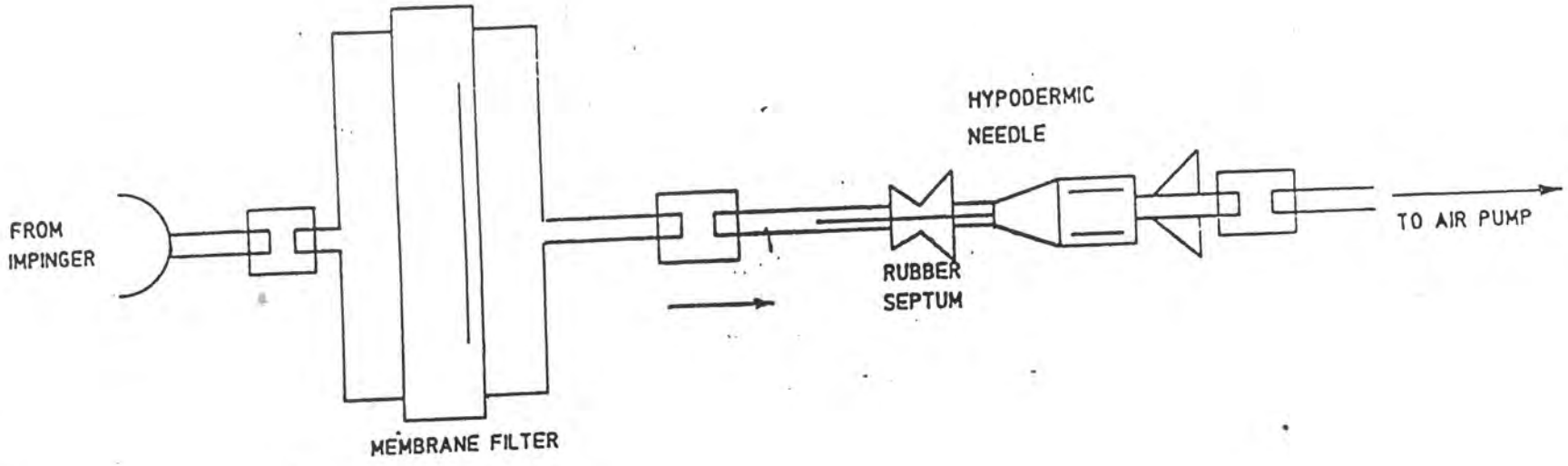

FIG. 2.0 CENTRAL ORIFICE FLOW CONTROL

1.0 TITLE

Method for determination of Nitrogen Dioxide in the Atmosphere (Sodium Arsenite method).

2.0 PURPOSE

The purpose is to lay down an uniform and reliable method for sampling and analysis nitrogen dioxide in ambient air.

3.0 PRINCIPLE

3.1 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 n m.

3.2 The nominal range of the method is 9 to 750 µg NO_2/m^3 (0.005 to 0.4 ppm)[3]. The range of the analysis is 0.04 to 2.0 µg 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 µg/NO_2/m^3 (0.005 to 0.22 ppm). Nitrogen dioxide concentrations in the range of 420 to 750 µg/m^3 (0.22 to 0.4 ppm) are accurately measured by 1:1 dilution of the collected sample.

3.3 Based on results from a collaborative study, the withiO 2aboratory standard deviation is 8 µg/m^3 (0.004 ppm) and the between laboratory standard deviation is 11 µg/m^3 (0.006 ppm) over the range of 50 to 300 µg NO_2/m^3 (0.027 to 1.16 ppm)[4].

3.4 Based on results from a collaborative study, the method has an average bias of -3% over the range of 50 to 300 µg NO_2/m^3 (0.027 to 0.16 ppm)[4].

4.0 SCOPE

This method is applicable to 24 hours integrated sampling of NO_2 in ambient air.

7.1.4 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.

7.1.5 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,[6] 10 mm (3/8 in.) long, used as a critical orifice. (Most 27 gauge needles will give flow rates in this range).

7.1.6 Air Pump - Capable of maintaining a vacuum of at least 0.6 atmosphere (450 torr) across the flow control device. [This value is based on the critical pressure differential, 0.53 atmosphere (400 torr)[6], plus a safety factor to allow for variations in atmospheric pressure and minor variations in pump performance].

7.1.7 Flowmeter - Properly calibrated flowmeter for measuring air flow rates in the range of 150-250 cm^3/min. The use of a mass flowmeter 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 (see 10.1).

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

7.2 Analysis

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

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

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

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

8.0 REAGENTS

All reagents should conform to ACS specifications for reagent grade materials unless otherwise specified.

8.1 Sampling

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

8.1.2 **Sodium Hydroxide.**

8.1.3 **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 not take internally.

8.1.4 **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.

8.2 Analysis

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

8.2.2 **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.**

8.2.3 **Hydrogen Peroxide, 30%.**

8.2.4 **Phosphoric Acid, 85%.**

8.2.5 **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.

8.2.6 **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.

8.2.7 **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.

9.0 PROCEDURE

9.1 Preparation of Calibration Graph

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

9.1.2 Sodium Nitrite Stock Solution (1000 µg NO_2^-/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 NO_2^-/ml is obtained. The amount of $NaNO_2$ to be used if, the assay percent is less than 100%, is calculated as follows :

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

Where :

G = Amount of $NaNO_2$, 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.

9.1.3 **Sodium Nitrite Working Standard (1.0 µg NO_2^-/ml)**

9.1.3.1 **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 NO_2^-/ml.

9.1.3.2 **Solution B** - Pipet 25 ml of solution A into a 250 volumetric flask and dilute to volume with absorbing solution. This contains 1 µg NO_2^-/ml. Prepare fresh daily.

9.2 Calibration

9.2.1 Flowmeter - Calibrate the flowmeter against a calibrated flow measurement standard, such as a wet test meter, bubble flowmeter, or other reliable volume measurement standard. Calibrate in units of standard cm^3/min (i.e., corrected to 25°C and 760 torr).

9.2.2 Absorber - Calibrate the polypropylene absorber (see 8.1.2) by pipeting 50 ml of water or absorbing reagent into the absorber. Scribe the level of the meniscus with a sharp object, mark over the area with a felt-tip marking pen, and rub off the excess.

9.2.3 Spectrophotometer

9.2.3.1 Prepare calibration curve using 1 µg/ml working standards (see 9.1.3.2).

9.2.3.2 In accordance with the analytical procedure given in 9.4, measure and record the absorbance for each calibration standard (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20 µg NO_2^-.

9.2.3.3 Plot absorbance (y-axis) versus the corresponding concentration in µg NO_2^-/50 ml final solution (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve.

9.3 Sample Collection

9.3.1 4-Hourly Sampling

9.3.1.1 Assemble the sampling apparatus (Figure 1) 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.

9.3.1.2 Add exactly 30 ml of absorbing reagent to the calibrated absorber.

9.3.1.3 Disconnect the funnel, connect the calibrated flowmeter, measure the flow rate before sampling and record as F_i. 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.

9.3.1.4 Sample for 4 hrs. Record the exact sampling time in minutes at t_i.

9.3.1.5 Measure the flow rate after the sampling and record as F_f.

9.3.1.6 Seal the collected samples and transport to the laboratory for analysis.

9.3.2 24-Hourly Sampling

9.3.2.1 Assemble the sampling apparatus (Figure 1) at the sampling site. Components upstream from the absorber may be connected, where required, with Teflon^R tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with Tygon^R, Teflon^R, or polypropylene.

9.3.2.2 Add exactly 30 ml of absorbing reagent to the calibrated absorber.

9.3.2.3 Disconnect the funnel, connect the calibrated flowmeter, measure the flow rate before sampling and record as F_i. If, the flow rate before sampling is not between 180 and 220 cm^3/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.

9.3.2.4 Sample for 24 hrs. Record the exact sampling time in minutes at t_s.

9.3.2.5 Measure the flow rate after the sampling period and record as F_f.

9.3.2.6 Seal the collected samples and transport to the laboratory for analysis.

9.4 Analysis

9.4.1 Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorber. Mix thoroughly.

9.4.2 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.

9.4.3 Prepare a blank in the same manner using 10 ml of unexposed absorbing reagent.

9.4.4 After a 10 min color development interval, measure and record the absorbance at 540 nm against the blank.

9.4.5 Determine µg NO_2^- from the calibration curve (see 9.2.3.3).

9.4.6 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.

9.4.7 A randomly selected 5-10% of the samples should be reanalyzed as apart of an internal quality assurance program.

9.5 Sampling Efficiency

The overall average efficiency is 82% from 40 to 750 µg NO_2^-/m^3 (0.02 to 0.4 ppm)[3]

10.0 CALCULATIONS

10.1 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, m^3
F_1 = Air flow rate before sampling, cm^3/min
F_f = Air flow rate after sampling, cm^3/min
t_s = Sampling time, min
10^{-6} = Conversion of cm^3 to m^3

If, the temperature and pressure conditions at the time of the initial and final air flow rate measurements are substantially different from the conditions under which the flowmeter was calibrated, appropriate corrections to the flow rate measurements may be made to improve the accuracy of the resultant NO_2 concentration measurement. The mathematical form of these corrections depends on the type of flowmeter used; consult an appropriate reference for guidance.

10.2 NO_2^- Concentration in Analyzed Sample - Determine µg NO_2^-/ml graphically from the calibration curve or compute from the slope and intercept values (see 9.3.3).

10.3 NO_2 Concentration in Air Sample - Calculate as µg of NO_2 per cubic meter of air as follows :

$$\mu g\ NO_2/m^3 = \frac{\mu g/NO_2^- \times V_s}{Va \times 0.82 \times V_t} \times D$$

Where :

$\mu g/NO_2^-$ = NO_2^- concentration in analyzed sample
Va = Volume of air sample, 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

10.4 The NO_2 concentration may be calculated as ppm using :

$$ppm\ NO_2 = (\mu g\ NO_2/m^3) \times 5.32 \times 10^{-4}$$

11.0 REFERENCES

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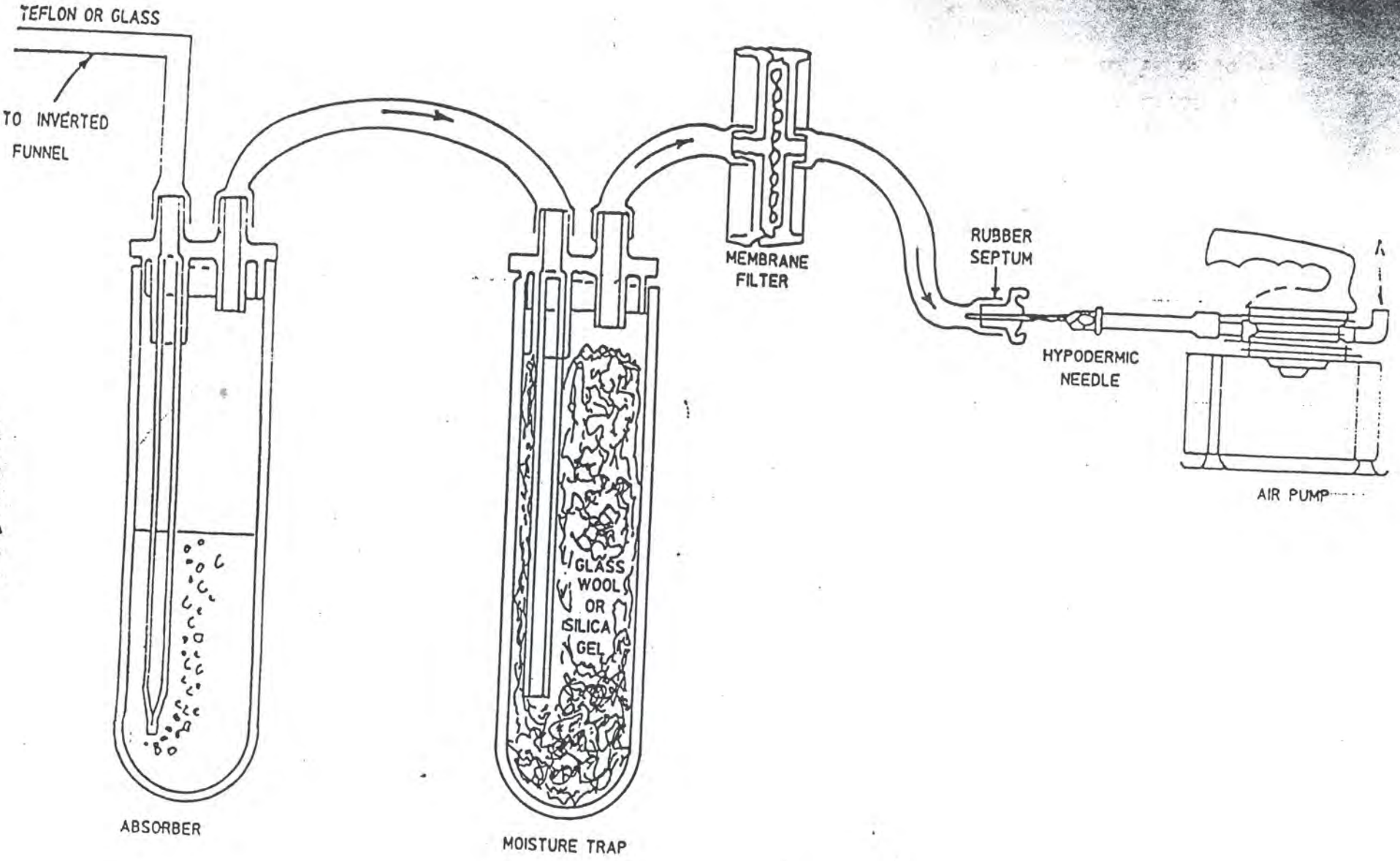

NO_2

FIG. 1 SAMPLING SYSTEM

PROCEDURE FOR PREPARATION OF DISTILL WATER USING DISTILLATION APPARATUS

1. Add some glass beads or boiling chips in the clean distillation flask.
2. Take 1.5 litre tap water in the distillation flask.
3. Keep The distillation flask on the heating mantle.
4. Connect T-shaped glass tube with distillation flask.
5. Connect Condenser with T-shaped glass tube..
6. Regulate the water supply through the inlet and outlet of the Condenser.
7. Set the temperature at heating mantle at 150°C using regulator.
8. Collect the distillate (distilled water) in such a manner that it should not be exposed to atmospheric CO_2 of the ambient environment.
9. Check the Conductivity of the distillate, if the Conductivity of the distillate is more than 3μmho/cm at 25 ° C, then re-distillate the distilled water collected and test the Conductivity. In re-distillation the Conductivity need to be achieved less than 3μmho/cm.
10. Store the distilled Water in the clean glass/Polyethylene/ other suitable plastic container which do not affect the quality of the water. No air space need to be left in the Container before sealing the bottle.

Precaution:-

1. Need to be proper greased the various joints of the distillation assembly.
2. Cold water need to be circulated through the condenser and it should be stopped after one hour of stopping power supply to heating mantle.
3. Glass beads or boiling chips need to be added in the boiling water during distillation to avoid bumping and effective heat transfer.