AIR QUALITY MONITORING AND CONTROL

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BIBLIOGRAPHY
FOREWORD

The World Health Organization has been developing a global air monitoring project since the early seventies. Starting as a pilot project in 1972, the project began to expand rapidly in 1975 with financial support from the United Nations Environment Programme; today about 50 countries participate as part of the Global Environmental Monitoring System.

To assist Member States with the training of staff for air monitoring operations interregional courses are organized periodically as part of the project. One of these was held in Bangkok in 1977 at Chulalongkorn University. The lecture notes from this course form the basis of this document.

These notes had been prepared by staff from the WHO Collaborating Centre on Air Pollution Monitoring for the Western Pacific Region in Brisbane, Australia, and they also subsequently prepared the final draft for this manual. An earlier draft had been reviewed by Dr Verduyn, Ministry of Health and Family, Brussels, Belgium, Dr Sundaresan, National Environmental Engineering Research Institute, Nagpur, India, Dr R. Hoskadam, Pan American Centre for Sanitary Engineering and Environmental Sciences, Lima, Peru, Dr Kirov, Western Pacific Regional Centre for the Promotion of Environmental Planning and Applied Studies, Kuala Lumpur, Malaysia, and Mr Kohler, World Meteorological Organization, Geneva, Switzerland. Where possible all advice given has been incorporated and their contribution is herewith gratefully acknowledged.

This document is intended primarily for technical staff involved in the day to day operations of an air monitoring network. The information presented in the text is for a large part concerned with various aspects of air monitoring. In order however to place the subject of air monitoring in its proper perspective with regard to the whole subject of air quality management, additional chapters have been added on "Sources of Air Pollution and Trends", "Effects of Air Pollution" and "Transport, Dispersion, Transformation and Degradation of Pollutants". The purpose of this manual is to elaborate on various technical details of an air monitoring operation for the purpose of improving the quality and to promote a more uniform approach among various national agencies. Note should also be taken of various other WHO publications in the field of air pollution which have been listed in the bibliography along with other pertinent references. In this connexion, the reader's attention is particularly drawn to WHO Offset Publication No. 24, Selected Methods of Measuring Air Pollutants, which presents the most commonly used procedures for measuring the more common types of air pollution.

The preparation and publication of this manual was supported with funds made available from UNEP's Environment Fund. Also the effort made by the authors, Dr G.J. Cleary, Mr B.R. Thiele and Dr P.M. Ninno in the preparation of this document and the numerous figures is hereby gratefully acknowledged.

It is expected that users of this manual will draw our attention to the difficulties they encounter in applying the techniques mentioned in this document, and make suggestions for improvement. Any comments regarding this document should be addressed to Director, Western Pacific Regional Centre for the Promotion of Environmental Planning and Applied Studies, P.O. Box 2550, Kuala Lumpur, Malaysia.

It should also be emphasized that the views expressed should not be construed as representing either a decision or a policy of the World Health Organization or the United Nations Environment Programme.
1. INTRODUCTION

1.1 General Considerations

Before any study of measurement techniques in Air Pollution monitoring can be undertaken, it is first necessary to gain an understanding of the problems involved, and to consider the basic theory of the equipment to be used.

In ambient air pollution monitoring the material to be measured (that is, the pollutant) is present in extremely low concentrations, in the range of parts per million \((10^{-6})\) or parts per billion \((10^{-9})\). In terms of weight per volume, this is equivalent to milligrams or micrograms per cubic metre. The significance of this may be better appreciated by considering that 1 part per million of a gas is equivalent to one cubic metre of it mixed into air space 100 metres long, 100 metres wide and 100 metres high. This pollutant must be identified and measured accurately and specifically.

Further, the pollutant is not contained in a pure, consistent medium, the air mass will contain in addition, varying quantities of water vapour solid particles and other pollutants which may or may not interfere with the analysis. Any analytical method used must record that pollutant only, or, at least, any interference caused by another pollutant must be capable of being measured or nullified.

The air sampled must also provide a proper representation of the area under study. If the air sample is not representative, then the results obtained will not indicate air quality in the area, regardless of how accurate, specific and sensitive the analysis is, or how competent the analyst. This subject is covered in depth in WHO Offset Publication No. 33, "Air Monitoring Design For Urban and Industrial Areas".

Finally, proper techniques of sample collection and analysis must be employed. Suitable techniques are discussed in considerable detail in WHO Offset Publication No. 24, "Selected Methods of Measuring Air Pollutants".

Air monitoring can be divided into two components, air sampling, which involves the removal of a known volume of air from the atmosphere, and analysis of the air sample to determine the concentration of an air pollutant in that sample.

In general terms, air sampling can be done by collecting a series of known volumes of air, one after the other and analyzing the result of each sample. Such a procedure is generally referred to as a manual method and involves transporting the samples from the sampling location to the central laboratory for analysis.

In another procedure, air is continuously drawn from the atmosphere and led into some type of detector device which analyzes the air continuously. Such instruments usually provide an electrical signal which is recorded using a strip chart recorder or some other data recording device. Such methods are called continuous methods or automatic methods. For the purpose of this manual, we shall refer to manual methods and automatic methods.

There are a number of variations, for example, where part of the manual operation has been automated; there also exist instruments which analyze a series of distinct air samples, such instruments are sometimes referred to as semi-automatic.

There are advantages and disadvantages to using manual methods and automatic methods. Manual methods generally are more labour-intensive, but require less capital investment. They can be more sensitive, in that a larger volume of air can be taken in each sample. Very often they can utilize a considerable amount of existing equipment, facilities and personnel. Automatic methods require a much higher capital investment and also a higher level of operating staff. More important than that, their operating and maintenance costs are generally much higher than for a manual procedure. Their advantage however is that they provide continuous data which is required for certain monitoring applications (see also WHO Offset Publication No. 33)

Also for the measurement of some pollutants there are really no good manual methods, for example,
for ozone.

Many monitoring networks begin as manual operations and gradually introduce some automatic instruments to suit the particular objectives for which the air monitoring is carried out. It should be noted however that for certain situations manual operations may be preferred over automatic instruments and vice versa. It would be quite erroneous to assume that either one or the other would be better under all circumstances. In other words, both have their advantages and disadvantages and these will have to be weighed in the light of the objective(s) for which the air quality monitoring network is established or further developed.

1.2 The Gas Laws

When analyzing an air sample for a pollutant gas, two measurements must be made, the weight of pollutant collected and the volume of air in which it is contained. Both of these must be determined as accurately as possible if a reliable answer is to be obtained.

1.2.1 Gas Volumes

The volume of a gas, as measured, does not provide a measure of the quantity sampled, unless temperature and pressure are prescribed, since the gas volume changes with changes in temperature and pressure. This is defined in two of the fundamental gas laws, Boyle's Law and Charles' (or Gay Lussac's) Law.

1.2.1.1 Boyle's Law and Charles' Law

Boyle's Law states: "The volume of a given mass of a gas at constant temperature varies inversely as the absolute pressure".

Charles' Law states: "The volume of a given mass of a gas at constant pressure varies directly as the absolute temperature".

These two laws may be combined and expressed mathematically:

\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R
\]

or

\[
V_1 = V_2 \cdot \frac{P_2}{P_1} \cdot \frac{T_1}{T_2}
\]

where \(P_1, P_2\) are the gas pressures in millimetres of mercury or kilopascals
\(T_1, T_2\) are the gas temperatures in ° Kelvin (or ° Absolute)
\(V_1\) = volume of the gas at pressure \(P_1\) and temperature \(T_1\)
\(V_2\) = volume of the gas at pressure \(P_2\) and temperature \(T_2\)
\(R\) = the universal gas constant

1.2.1.2 Standard Temperature and Pressure

Atmospheric temperature and pressure vary continuously at all places throughout the world. In any air quality monitoring programme ambient air samples will therefore be collected over a range of temperatures and pressures. Because of this, a standard reference of temperature and pressure is required if the result, expressed in terms of a measured weight of pollutant per measured volume of air (weight/volume), is to have a consistent meaning.

Monitoring results submitted under the GEMS/Air programme are
to be reported under specified conditions of 25°C temperature and 760 millimetres of mercury (or 101.3 kPa) pressure. In other places, 0°C and 760 millimetres of mercury is sometimes used. In referring a gas volume to these standard conditions, it should be noted that absolute zero temperature is equal to -273°C, so that 25°C is equal to 298° Absolute, or 298 K. So, for data to be included in the GEMS/Air programme:

\[ V_{\text{standard}} = V_{\text{measured}} \times \frac{P}{760} \times \frac{298}{273} \text{°C} \]

(Where pressure is measured in kPa, the figure 760 would be replaced by 101.3).

This correction is necessary when pollutant concentrations are expressed on a weight/volume basis (i.e. in milligrams per cubic metre or micrograms per cubic metre), since the weight of pollutant will remain constant, while the volume of the sample will change with changes in temperature and pressure.

This correction is not necessary when pollutant concentrations are expressed on a volume/volume basis (i.e. parts per million or parts per billion), since the volume of the pollutant and the volume of sample will change with changes in temperature and pressure. However, the percentage change will be the same in each case, since all gases obey the gas laws described above. Hence, the volume to volume ratio of the two will remain the same.

When samples are collected over a 24 hour period, some difficulty may be experienced in determining the sample temperature and sample pressure to be used in the calculation. There are several courses which might be followed. A reading of temperature and pressure may be taken regularly during the 24 hour period, or continuously recording instruments measuring atmospheric temperature and pressure (thermographs and barographs) may be operated. Mean temperature and pressure may be calculated from the readings, or deduced from the recorder charts. However, it is usually of sufficient accuracy to obtain the maximum and minimum temperature and pressure recorded each day by the Bureau of Meteorology, and take the mean of these. This should not introduce significant errors in the result.

(An error of 1°C in temperature induces an error of \( \frac{1}{273 + 25} \), or approximately 0.3 percent in the measured volume, and an error of 5 millimetres of mercury in pressure induces an error of \( \frac{5}{760} \), or approximately 0.65 percent.)

Example:

A 24 hour sample of ambient air is found to contain 37 micrograms of Sulphur dioxide in a measured volume of 297 litres of air. The temperature during the 24 hours ranged between 10°C and 24°C, and the barometric pressure ranged between 755 millimetres of mercury and 761 millimetres of mercury. What mean concentration of sulphur dioxide should be reported to the GEMS data bank?

1. Mean temperature

\[ t = \frac{t_{\text{max}} + t_{\text{min}}}{2} = \frac{10 + 24}{2} = 17°C \]

2. Mean pressure

\[ p = \frac{p_{\text{max}} + p_{\text{min}}}{2} = \frac{755 + 761}{2} = 758 \text{ millimetres of mercury} \]
3. Volume of sample at 25°C and 760 millimetres of mercury

\[ V_{st} = 297 \times \frac{758}{760} \times \frac{293}{273} + 17 \text{ litres} \]

\[ = 304 \text{ litres} \]

\[ = 0.304 \text{ cubic metres} \]

4. Concentration of sulphur dioxide

\[ = \frac{37}{0.304} \]

\[ = 122 \text{ micrograms per cubic metre.} \]

1.2.1.3 **Avogadro's Law**

The volume occupied by 1 gram-molecule of a gas is the same for all gases under the same conditions of temperature and pressure. The expression \( PV/T \) must have the same value therefore, for 1 gram molecule of any gas. This is usually represented by \( R \), which gives the general gas equation.

\[ PV = RT \]

or, for \( n \) gram-molecules of gas

\[ PV = nRT \]

\( R \) is known as the universal gas constant. In practice, it is found to be 22.414, at temperature of 0°C, 760 millimetres of mercury pressure with the volume measured in litres, or 24.45 at 25°C, and 760 millimetres pressure.

1.3 **Conversion Formulae**

In converting from "volume per volume" to "mass per volume", use is made of the gram-molecular volume relationship stated in Avogadro's Law, namely, that the volume occupied by one gram molecular mass of a gas at a temperature of 293K and a pressure of 760 millimetres of mercury is equal to 24.45 litres, (or 22.40 litres at 0°C and 760 millimetres of mercury).

Thus:

\[ (\text{parts per million}) \times \left( \frac{M}{24450} \times 10^6 \right) = \text{micrograms per cubic metre under these standard conditions.} \]

Where \( M \) is the gram molecular mass of the gas.
2. SAMPLING TRAINS

2.1 General Considerations

A sampling train has four essential elements. First, a sampling line or opening through which the ambient air is sampled. Next, a pump to extract the air sample, and a means to measure its volume. Finally, a device by which the pollutant under study is collected from the air sample for analysis. These four elements may be connected together by tubing, or may be constructed as a single, integral unit.

If sampling is to occur through a sample line, the material of construction of this line must be considered, to ensure that absorption or diffusion errors are not introduced. Nylon and polypropylene are suitable materials for sample lines in most cases, although teflon is the only material satisfactory for ozone sampling lines. Glass tubing may also be used, with joints constructed by inserting the ends of the two pieces into a short piece of plastic tubing and butting them together, so that the air sample only contacts glass.

Flowrate through the sample line should be such that the air sample spends a minimum of time in the line, reducing the time available for sample degradation. The line should be kept free of particulate material, either by protecting the inlet with a filter, by regular cleaning of the line, or by replacing it at regular intervals. If a filter is used it must be cleaned or changed regularly to prevent a pressure drop from developing across it. These precautions are taken to prevent reactions from occurring between the sample and the particulate matter.

In practice, the "collecting" portion of the train is placed in the sampling line ahead of the pump and volume measuring device. In this way, the concentration of pollutant in the air sample cannot be affected by contact with these two units.

Sample volume may be measured in either of two ways, by the use of a gas meter or by measuring flow rate and sampling time, and calculating the volume from these.

Collection of the pollutant for analysis may be achieved in several ways. Gases may be absorbed or reacted into a solution, where they may be subjected to further chemical reaction to produce a coloured material. The intensity of this colour is used to determine the concentration of pollutant in the air sample. An example of this is seen in the determination of sulphur dioxide by the pararosaniline method. Or, in a similar system, the collecting reagent may develop a colour without further reaction, as, for example, in the determination of nitric oxide by the Saltzman method. Both of these methods are described in detail in "Selected Methods of Measuring Air Pollutants".

Alternatively, the gaseous pollutant may be adsorbed on to a solid medium such as activated charcoal, silica gel or some of the porous polymer materials used in gas chromatography. In this case, the pollutant must be removed from the adsorbent, either by washing it out with a suitable solvent or by eluting it into a gas stream with heat.

Solid particles are usually removed from the air sample by filtration on to a solid medium. In high volume sampling the sample train is a single unit, comprising a filter, exposed to the air within the sampler housing, with the pump and motor attached below. In the basic sampler, there is no permanent flow or volume measuring device used. Sample volume is determined by measuring flow rate at the commencement and the end of the sampling period and using the mean of these in the calculation.

2.2 Air Pumps

There is a wide variety of suitable electrically driven pumps available for use in air sampling, utilizing different operating principles. The main categories of pumps and some of their advantages and disadvantages are shown in Table 1. Table 2 lists a number of pump types together with their airflow characteristics under free-flow conditions and their most common application in air pollution monitoring.

The pump flow capacity required is determined by the total volume of air to be
## Table 1 - Advantages and Disadvantages of Pump Types

<table>
<thead>
<tr>
<th>Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2. Produces constant volumetric air flow so that output flow rate can be</td>
<td>2. Working parts such as check valves and piston rings can wear, creating</td>
</tr>
<tr>
<td></td>
<td>controlled by regulating pump motor speed through applied voltage.</td>
<td>leakage and other problems.</td>
</tr>
<tr>
<td></td>
<td>2. No seals as with piston pumps.</td>
<td>2. Operates only a limited suction pressure.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Material of construction of diaphragm or bellows limited to neoprene or</td>
</tr>
<tr>
<td></td>
<td></td>
<td>stainless steel.</td>
</tr>
<tr>
<td></td>
<td>3. Can operate at high suction pressures.</td>
<td>3. Slippage between moveable parts.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Poor self-lubrication at low vacuum.</td>
</tr>
<tr>
<td>Rotary Lobe Pump</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotary Vane Pump</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifugal Pump</td>
<td>1. Large range of flow rates.</td>
<td>1. Unsuitable for small flow rates.</td>
</tr>
<tr>
<td></td>
<td>2. No close clearances on moving parts.</td>
<td>2. Gas flow is highly turbulent.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Noisy in operation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Relatively low suction pressure.</td>
</tr>
<tr>
<td>Turbine Blower</td>
<td>1. Large flow rates only.</td>
<td>1. Noisy in operation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Low suction pressure.</td>
</tr>
</tbody>
</table>
Table 2 - Air Flow Under Free-flow Conditions and Applications of Different Pump Types

<table>
<thead>
<tr>
<th>Type</th>
<th>Air flow under free-flow conditions in litres per minute</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum*</td>
<td>Minimum*</td>
</tr>
<tr>
<td>Diaphragm Pump</td>
<td>70</td>
<td>4</td>
</tr>
<tr>
<td>Piston Pump</td>
<td>70</td>
<td>25</td>
</tr>
<tr>
<td>Vane Pump</td>
<td>1060</td>
<td>10</td>
</tr>
<tr>
<td>Centrifugal Blower</td>
<td>3600</td>
<td>400</td>
</tr>
</tbody>
</table>

moved, together with restrictions and obstructions such as critical orifices and filters in the sampling train. As the resistance in the sampling train increases the pressure at the intake to the pump drops, and pump performance decreases. When a pump is being selected for a particular sampling train, its capacity must be determined at the maximum line vacuum to be expected, to ensure that the pump will sample the required volume at this pressure. As a general rule, any pump which will pump the required volume of air under the worst pressure conditions is satisfactory for a particular sampling situation. Diaphragm pumps are most frequently used, because of the wide range of capacities available, their low cost and easy maintenance. However, sampling trains which include filters and those with critical orifices which develop particular high resistances may require some form of carbon vane or piston pump.

Other characteristics to be considered when selecting a pump include the maintenance requirements, both the frequency and type. For example, how often do carbon vanes, diaphragms, or brushes need to be replaced? How noisy is it? Can it operate in warm climates? Does the pump have some kind of calibrated orifice intake or pressure gauges fitted to the air intake and outlet, from which the flow rate can be calculated?

2.3 Determination of Air Volumes

The volume of air sampled may be determined by one of three methods. Firstly, by the use of a calibrated gas meter, secondly by collecting the sample into a vessel of known volume, or thirdly, by collecting the sample at a measured flowrate, and recording the sampling period.

2.3.1 Gas Meters

These are usually the so-called positive displacement gas meters, described in 2.3.1.1 and 2.3.1.2. It should be noted that these are usually of low flow rate capacity, and cannot be used with high-volume, suspended particulate matter samplers.

2.3.1.1 Wet Gas Meters

The wet gas meter is one of the standard instruments for measuring total gas volume. It consists of a cylindrical case containing a rotor drum suspended in a liquid (usually water) on a horizontal axis. This drum is divided into four exactly equal spiral compartments by metal
vanes. The gas enters through an opening near the axis of each chamber, and exits through another opening near the outside of the case. The pressure of the incoming gas causes the drum to rotate, and this rotation is recorded by rotating hands on the face of the drum (Figure 1). These meters measure gas saturated with water vapour, at the temperature of the gas meter.

2.3.1.2 Dry Gas Meters

In this type of meter, the entering gas stream moves diaphragms or bellows. This movement is transferred by a crank to the rotating hands of the scale, or to a digital reading device. (Figure 2)

In practice, dry gas meters are more usually used than wet gas meters. First, they are lighter and easier to carry, second they do not require the same firm, level surface for mounting. They are not as accurate as wet gas meters, however.

2.3.2 Containers

2.3.2.1 Sampling Tubes and Bottles

"Grab Samples", that is samples taken over a very short time period, may be collected in a gas sampling tube, an evacuated vessel, a bag constructed from a suitable plastic sheeting or a glass syringe.

The gas sampling tube (Figure 3) consists of a glass or plastic vessel of known volume, equipped with a stop at either end. A volume of air equal to 8 or 10 times the volume of the vessel is sucked through by
means of a squeeze bulb or pump so that the air in the vessel is completely replaced by ambient air. The two taps are then closed to retain the sample. A simple variation of this which may be used when water insoluble pollutants are to be sampled, is to carry to the site a bottle of known volume filled with water. The water is emptied out (and replaced by ambient air), the bottle sealed, and returned to the laboratory.

Alternatively, a stout bottle or other vessel may be evacuated, sealed (either with a stopper and glass tube, drawn to a tip and sealed, or with a stopper and glass tube fitted with rubber tubing closed with a spring clip) and taken to the sample site. The seal is broken, and the vessel fills with ambient air. In measuring the volume of the sample, it must be remembered that evacuation does not remove all the air from the vessel, and allowance must be made for the air which remains when calculating sample volume. Further, evacuated vessels may implode easily, hence they should always be protected during storage or handling. This may be done by placing the vessel in a cardboard carton, packed around with rags, with only the neck showing at the top.

The safest practice is to evacuate the vessel partially, rather than to strive for a high vacuum. In this way, the risk of implosion is lessened. The pressure in the vessel must be measured at the time of sampling, since the volume of sample collected now becomes:

\[ V_{\text{sample}} = V_{\text{flask}} \times \frac{P_{\text{atmos}} - P_{\text{flask}}}{P_{\text{atmos}}} \]

2.3.2.2 Sampling Bags

The sample may be collected in a plastic bag, provided that a suitable plastic material is used. Plastic bags have many advantages, including lightness, resistance to breakage, ready variability in size and ease in handling. Much larger samples may be collected in this way. Bags of varying sizes are available commercially, or they may be made up as required. The plastic sheeting is cut to size, folded into the bag shape and edges sealed with P.V.C. or similar tape. A small piece of tubing or a tyre valve is sealed into one corner of the bag, making sure that a good seal is obtained. The bag is first rolled tightly to exclude all air, then unrolled and the sample admitted by a hand or motor driven pump or a squeeze bulb. The bag should then be squeezed empty and refilled, to ensure that the contents are representative of the ambient air.

2.3.2.3 Syringes

Small samples of air, of 100 c.c.s or less, may be collected in a glass syringe. This technique is only useful where a very sensitive method of analysis is available, since only small samples can be collected in this way.

Whatever the grab sampling technique used, care must be taken to use a suitable material of construction for the sample container. It must be impervious to the pollutant to be sampled, so that none is lost through permeation through the walls. The pollutant must not be absorbed or adsorbed into the walls, or react with them. Similar precautions must be taken with the pump or squeeze bulb, so that it does not alter the pollutant concentration. The pump or squeeze bulb should always be downstream of the collecting medium.

Suitability of the container may be determined by filling several containers with air containing the same known concentration of pollutant, and constructing a decay curve, measuring the fall off in concentration with time, by analysing individual containers at set time intervals. In some cases, the container may be conditioned by repeating
this procedure several times, until no decay curve is apparent.

2.3.3 Measurement of Gas Flowrate

2.3.3.1 Orifice Meters

An orifice meter is a device which has an accurately machined and drilled plate with the hole concentric with the pipe in which it is mounted, fixed between two flanges. Pressure tappings are installed, one upstream and one downstream of the orifice plate, and connected to a manometer or equivalent pressure measuring device (Figure 4).

![Figure 4 - Orifice Meter](image)

If the performance of an orifice meter is to be predicted without calibration, certain definite construction and design standards must be met. Details of these are to be found in British Standard 1042: Part 1, Methods for the Measurement of Fluid Flow in Pipes. Otherwise, it may be calibrated against a wet gas meter or other standard flow device.

Meters of this type are used to calibrate the flowrate through a high volume sampler. In this case, however, there is no pipe upstream of the orifice.

2.3.3.2 Gas Flowmeters

The gas flowmeter is an easily constructed device which utilizes a small capillary tube in place of the orifice (Figure 5).

![Figure 5 - Gas Flowmeter](image)
The difference in pressure created upstream and downstream of the capillary is recorded by a manometer, which may be graduated in litres per minute if desired. These instruments must be calibrated against a standard gas meter or a calibrated flow measuring device, as there is no way in which their characteristics may be accurately predicted.

2.3.3.3 Critical Orifice Flow Controllers

When a gas flows in a pipe which has a converging nozzle included in it, for any given set of upstream conditions the rate of discharge of the gas from the nozzle will increase for an increase in the pressure drop (ΔP) across the nozzle, until the linear velocity in the throat reaches the velocity of sound. Under this condition, flow depends on the upstream pressure only, and since this remains constant during ambient air sampling, the flowrate has a constant value once the critical pressure is reached, regardless of how the downstream pressure varies below the critical point. This is illustrated in the graph below (Figure 6). Note that the lower the critical flowrate, the lower ΔP is required. In practice, the pressure in the downstream line should be kept well below the critical pressure, so that the flowrate is independent of minor changes in pump velocity.

Critical orifices must always be protected by a filter of low pore size, since dust particles in the incoming stream can readily restrict the small orifice, and alter the flow characteristics.

Hypodermic needles may be used as critical orifices, as shown in Figure 7. (A 22 gauge needle (0.394 mm I.D.) 2.5 cm long gives a flow of about 1 litre per minute, a 23 gauge needle (0.318 mm I.D.) 1.5 cm long gives a flow of about 0.5 litre per minute, and a 27 gauge needle (0.191 mm I.D.) 0.9 cm long gives a flow of about 0.2 litre per minute.)

Critical Orifice Flow Control

Figure 6

Critical Orifice Flow Control

Figure 7
2.3.3.4 Rotameters

The rotameter is an apparatus (Figure 8) which measures the velocity of flow of gas by the height at which a float is carried by a stream of gas. It consists of a tapering glass or plastic tube mounted in a manner so that it can be levelled plumb. The gas enters at the lower end of the tube, and streams past a light float or ball. As the flow increases, the float rises into a region of larger diameter. The height to which the float rises depends on the velocity of the gas, and the density of the material of construction of the float.

![Figure 8 - Rotameter and Floats](image)

2.3.3.5 Mass Flowmeters

Electronic mass flowmeters offer the most advanced gas flow sensing equipment at present available. These units generate a signal which is proportional to mass flow by detecting heat transport in the gas stream.

The flowmeter comprises a flow sensing transducer, a digital readout and transducer-to-readout connection cable. The transducer consists of an electrically heated tube and an arrangement of thermocouples to measure the differential cooling caused by a gas passing through the tube. Thermoelectric elements generate a d-c voltage which is proportional to the rate of mass flow, depending on the mass flow and heat capacity of the particular gas.

Once the electrical signal from the transducer has been generated, it is "linearized" electronically to give a voltage which is directly proportional to the mass flow rate of gas. Generally, once a transducer output signal has been "linearized" during an air calibration procedure, the transducer can be used to measure flowrates of other gases by applying the appropriate conversion factor.

If the signal voltage is used only to indicate flow, the unit is a linear mass flowmeter. If the signal is used in conjunction with a reference signal and a controlling element, the unit becomes a mass flow...
2.3.4 Calibration of Volume and Flow Measuring Equipment

All volume and flow measuring equipment must be calibrated, at regular intervals. The primary standard for this type of calibration is the gas test bottle, a container carrying two fixed marks. The volume between these marks is determined by filling the bottle with water to the first mark, weighing, adding water up to the second mark and reweighing. The volume of the bottle is then determined from the weight difference and the density of water at that temperature. This volume may then be used to calibrate a test holder, a larger, gasometer type of vessel known as a Spirometer (Figure 9).

From these, a wet gas meter may be calibrated, and used as a standard gas meter. Calibration should be performed at a series of flow rates, up to the maximum rated flow rate for the meter, and a graph of calibration against flow rate prepared. This meter is then used to calibrate other gasmeters, rotameters or critical orifices.

Standard equipment to conduct these calibrations is usually available in towns where natural gas or process gas is supplied to homes and industry. The gas suppliers will have it as a means of calibrating their own meters. Otherwise spirometers are usually available from a hospital where they are used to measure lung function. In the absence of these, a satisfactory calibration can be made according to the method described in ASTM Method D1071-55, "Standard Methods for Measurement of Gaseous Fuel Samples".

Figure 9 - Schematic Drawing of a Spirometer
(By courtesy of NIOSH)
altering the motor voltage. At the same time, this calibrated flowrate may be
sensed and recorded directly on a readout meter, as illustrated in Figure 11(b).

The flow capacity of less than 100 litres per minute. They cannot be used to
calibrate high volume samplers, which draw in excess of 1 cubic metre per minute
(40 cubic feet per minute). These may be calibrated using an orifice plate
flowmeter designed to clamp on to the filter holder of the sampler. This
calibration may be related to the reading of a small rotameter which measures a
fixed fraction of the air passing through the blower.

High volume samplers currently supplied under the GEMS/Air programme
combine flowrate calibration with flowrate control and recording. In this case,
a small thermister flowrate probe, which must itself be calibrated by an orifice plate
flowmeter, is situated in the throat of the filter holder. This senses flow
changes, which are then restored to the original set value by the controller
altering the motor voltage. At the same time, this calibrated flowrate may be
continuously recorded on a recorder, mounted in the sampler housing. This is
illustrated in Figure 11(a).

These two methods are described in detail in Section 1.2 of "Selected
Methods of Measuring Air Pollutants".

In a more recent variation of the flow controller, the flow probe is
fitted into a calibration head, which clamps on to the filter holder. The flow is
sensed and recorded directly on a readout meter, as illustrated in Figure 11(b).

None of these calibrators provide a suitable primary standard. Each of
these methods must themselves be calibrated against a large capacity positive
displacement gas meter.
Figure 11 - High Volume Sampler Flow Control and Measurement

2.3.4.1 Gasmeters

A gasmeter measures the volume of gas which passes through it without regard for temperature or pressure, so that if the pressure and temperature vary from 0°C and 101.3 kPa, allowance must be made. They follow the combined gas laws:

\[
V_1 = V_2 \frac{P_2 T_1}{P_1 T_2}
\]

Where:
- \( V_1 \) = gas volume at S.T.P.
- \( V_2 \) = gas volume measured at meter
- \( P_1 = 760 \) millimetres of mercury
- \( P_2 \) = meter pressure in millimetres of mercury
- \( T_1 = 25°C = 298 \) K.
- \( T_2 \) = meter temperature in K.

Volume corrections due to meter pressure may be minimised if the gas meter is placed at the end of the line, that is, with the outlet at atmospheric pressure. It is essential that all sample lines and the sampling pump must be completely free of leaks.

2.3.4.2 Rotameters

Rotameter Scales are of two types, either a standard (0-10)
uncalibrated scale, or one calibrated in terms of a flowrate of air, either as litres per minute, cubic feet per minute or cubic feet per hour. In any case, they must be calibrated, or the calibration checked regularly, using a standard gas meter and stopwatch. Sufficient points on the scale must be checked to enable a calibration graph of flowrate against scale reading to be constructed.

There are three types of rotameter floats in normal use, as illustrated in Figure 8.

These read at the points shown, unless otherwise indicated on the scale. Floats are made in a range of materials of various specific gravity, including glass, stainless steel, and aluminium. The range of flowrates which a rotameter can measure may be varied by using floats of different specific gravity, but a separate calibration must be prepared for each float. It is generally preferred that the flowrate to be measured should be about 75 percent of the rotameter maximum flowrate.

Rotameters are sensitive to gas density, just as gasmeters are. In this case, the conversion formula is:

$$F_S = F_m \sqrt{\frac{P_s \cdot T_m}{P_m \cdot T_s}}$$

- $F_s$ = Flowrate at S.T.P.
- $F_m$ = Measured flowrate, at pressure $P_m$
- $P_s$ = Standard Pressure = 760 millimetres of mercury
- $P_m$ = Measured Pressure, in millimetres of mercury
- $T_s$ = Standard Temperature = 25°C = 298K
- $T_m$ = Measured Temperature in K

Again, corrections to be applied are minimized if the rotameter is placed at the end of the sampling line, that is, with its outlet at atmospheric pressure. Again, it is essential, that all sampling lines and the sampling pump must be completely free of leaks.

The bore and float of these instruments must be kept clean if the calibration is to be maintained. The unit should be dismantled completely, washed with a non-abrasive cleaner, flushed well with deionized water and dried before reassembly. Calibration of the reassembled unit should then be checked.

### 2.3.4.3 Bubble Flowmeters

Low flowrates, of the order of cc's per minute, may be measured by means of a bubble flowmeter (Figure 12), which can be constructed from readily available materials.

This consists of a graduated glass tube (e.g. a graduated pipette or a burette barrel) with a T piece on the end. A rubber bulb containing a weak detergent solution is fitted to the lower end of the T piece. In practice, the bulb is squeezed until the detergent level reaches the side arm thorough which the air stream enters. The air stream forms bubbles which are carried up into the graduated tube, and the passage of a single bubble timed, using a stopwatch. Volume flowrate of the airstream can be timed in this way.
2.3.4.4 Critical Orifices

Although these are cheap, useful devices, they suffer the disadvantage that they require frequent checking and calibration. They must always be protected by a filter from the incoming air stream, as any dust particles in this stream will either abrade the orifice, or collect in it and reduce the effective diameter. Care must also be taken that the filter does not block and hence alter the pressure on the upstream side of the orifice, since it is the upstream pressure which determines critical flow. The filter must satisfy three requirements. First, and most obvious, it must be capable of filtering solid particles from the air stream. Secondly, it must provide a minimum of resistance to air flow in the system. Thirdly, it must not react with any gaseous pollutant to be measured. These three requirements are best satisfied by the commercial membrane filters which provide inert filtration of submicron particles with little pressure drop across the filter. When sampling reactive gases, such as ozone, teflon membranes should be used.

Each orifice should be calibrated for a series of $\Delta P$ values, so that the critical pressure, that is, the pressure below which a constant flowrate occurs through the orifice, may be established with certainty. This calibration should be checked after each use.
3. SAMPLING AND MEASUREMENT - GASEOUS POLLUTANTS

3.1 Sample Collection

Gas and vapours follow the normal laws of diffusion and mix freely with the surrounding atmosphere. Samples representing the air in the immediate vicinity may therefore be collected for analysis. As previously discussed, these may be short-term "grab samples", or samples collected over a longer period, with analysis to determine either the average concentration over the sample period, or continuous analysis recording instantaneous concentrations.

Care must be taken to ensure that the sample is, in fact, representative, and that no loss of pollutant has occurred, either through chemical reactions between the components of the collected sample, absorption into the walls of the sample lines or sample container, by diffusion through them, or through leaks. In the case of grab samples, this may be determined by constructing a "decay curve", that is, by analysing the sample repeatedly over a period of time commensurate with the anticipated time delay between sampling and analysis, and constructing a curve of concentration against time. When a rigid container is used, the sample may be collected directly into an evacuated vessel containing the absorbent in which it is to be later analysed. But again, care must be taken to ensure that no degradation occurs in the period between sampling and analysis.

3.2 Absorption in Liquids

In air pollution studies, the concentration of pollutant gas to be measured is very small, so a large volume of air must be sampled before sufficient of the material is collected, if it is to be determined accurately by classical wet chemical methods. This may be conveniently done by bubbling the air sample through a liquid which will absorb the pollutant, either by dissolving it or reacting with it.

It is important to know the efficiency of collection of the absorber and of the absorbing medium, as well as verifying that a lengthy sampling period will not alter or destroy the material being collected (e.g. by oxidation).

3.2.1 Efficiency of Absorption

The efficiency of an absorber may be defined as the ratio of contaminant trapped by the device or absorbing fluid to the total amount of contaminant present in the air stream.

\[
\text{\% efficiency} = \frac{\text{ppm entering gas} - \text{ppm effluent gas}}{\text{ppm entering gas}} \times 100
\]

Collection efficiency is seldom 100 percent, but it is desirable that it should be kept as high as possible, particularly in air pollution studies, where initial concentrations of the pollutant are usually low. Collection efficiency may be found to be constant at a level less than 100 percent. In this case, only a correction factor needs to be applied.

It is also desirable that retention efficiency should be kept as high as possible. Retention efficiency is a measure of the ability of a collecting medium to retain collected material in a condition suitable for later analysis. For example, if sulphur dioxide is collected in water, an equilibrium condition is attained, with the sulphur dioxide in the gas stream in equilibrium with that dissolved in the water. Under these conditions, no further sulphur dioxide is collected. For this reason, potassium tetrachloromercurate solution is used to collect sulphur dioxide. These two form a loosely bound compound, from which sulphur dioxide is not readily lost back into the air stream being sampled.

3.2.2 Determination of Collection Efficiency

The collection efficiency and retention efficiency of any system must be tested before it is adopted for field use, by one of the following methods:
1. By using it to sample a prepared gas-stream of known concentration, and measuring the amount of material collected and retained in the system.

2. By comparing results obtained using the system, with those of a test device of known accuracy.

3. By introducing a known amount of material under study into the collecting device, and passing a purified air stream through it for an extended period. The amount of material remaining in the collector is determined, and compared with the initial amount added. In this way, the losses through volatilization or destruction of the material may be calculated.

4. By connecting a second (or third) unit in series after the collecting device and before the pump.

The contents of these collectors are analysed separately, with the results providing an indication of the collecting efficiency of each single collector. This will also indicate the number of collectors which should be used in series for adequate collection efficiency of the total system.

3.2.3 Factors Affecting Absorption Efficiency

The extent to which gas is absorbed in liquids is governed, in general, by some or all of the following factors:

(a) the degree of contact between the gas and the liquid, as determined by bubble size;

(b) the duration of contact between the gas and the liquid, as measured by the rate of gas flow and the length of the gas path through the liquid;

(c) the transfer coefficients or rates of diffusion between gas and liquid phases;

(d) the degree of solubility of the gas in the liquid;

(e) the rate of chemical reaction;

(f) the concentration of the reactant in the absorbing solution; and

(g) the temperature of the absorbing solution.

3.2.4 Liquid Absorption Equipment

Simple liquid absorption devices, as illustrated in Figure 13 and Figure 14 depend on washing the incoming gas stream in water or other absorbing reagent, which may act by either solution, absorbing the material by chemical reaction, or by colorimetric reaction in the absorbing vessel. They may be divided into main groups:

1. Simple gas wash bottles, where the length of travel of the air sample is equivalent to the height or length of the absorbing liquid in the device (Figure 13(a)). The efficiency of these devices may be increased by drawing the inlet tube into a jet to lessen the size of the incoming bubbles, or by incorporating a spiral into the unit, to increase the absorption path length. (Figure 13(b)).

2. Units incorporating a dispersion mechanism such as a porous (or fritted) glass disc or plate (Figure 13(c), 13(d)). Using these, a greater bubble surface area is exposed to the absorbing solution, thus increasing the efficiency of absorption. Efficiency may be further enhanced by including in the absorbing solution a material to lower surface tension, and encourage foaming. In this case, a fritted glass bubbler such as
that shown in Figure 13(e) may be used, taking care that the collecting liquid used does not overfill the lower "finger" of the bubbler. The bulb of the bubbler allows the collecting liquid to foam freely, without the liquid being carried over into the next unit of the bubbler train.

As an alternative to these, the sample may be drawn through an absorbing vessel packed with glass beads wetted with absorbing liquid (Figure 13(f) and 13(g)). In these collectors the surface contact between air and absorbent is increased as the air stream flows over the wetted glass beads.

Figure 13 - Gas Absorbing Bubblers

Bubblers may be connected in a series of two or more, to increase the collecting efficiency of the system. If this is done, it may be useful to analyse the contents of the bubblers separately, to maintain a check on the efficiency of the individual bubblers. In all cases, whether a single collecting bubbler, or a series of bubblers are used, an additional empty bubbler should be included before the pump or gas meter, to collect any liquid carried over in the gas stream, either as droplets or through equipment malfunction. This may be packed with silica gel or other absorbent if additional protection of equipment downstream of the collectors is required.

Absorbing bubblers may be purchased commercially or may be simply constructed from a test tube, glass tubing and a two holed stopper. Care must be taken that the stopper does not react with the absorbing liquid or the pollutant under measure. Stoppers may be protected by coating them with paraffin wax or a similar medium, or by punching the inlet and outlet tubes through a thin plastic sheet, and drawing the sheet around the stopper before it is inserted into the test tube.

3.2.4.1 Impingement

The Greenberg-Smith Impinger and midget impinger are widely used to entrain or absorb airborne pollutants by impinging a high velocity airstream on a surface submerged in an absorbing liquid. (Figure 14). A detailed specification of the midget impinger is shown.
in Figure 5.2 of "Selected Methods of Measuring Air Pollution".

In the Greenberg-Smith Impinger the airstream is drawn through an orifice 2.3 mm in diameter and impinged on a flat surface 5 mm distant, with a jet velocity of about 113 m/sec at a sampling rate of 28.4 litres per minute. The distance from the jet to the impinging surface may be held constant by accurately constructing the length of the inlet tube, so that it ends exactly 5 mm from the base of the impinger flask (as in Figure 14(a)) or by fixing an impinging plate 5 mm below the inlet jet (as in Figure 14(b)). Sufficient liquid must be present to cover the impinging surface to a depth of approximately 3 cm, 100 ml of liquid is usually sufficient.

The Midget Impinger is, as its name suggests, a small version of the Greenberg-Smith Impinger, approximately one-tenth the size and having one-tenth the flow rate. In this case, the orifice is 1 mm diameter, and 10 ml absorbing solution is used. The power required to draw the air sample through is much less, in fact it may readily be operated using a hand cranked pump.

The approximate range of usefulness of different absorbers is indicated in Table 3.
### Table 3 - Absorbers for Air Sampling

<table>
<thead>
<tr>
<th>Type of Absorber</th>
<th>Absorbent Capacity (ml)</th>
<th>Sampling Rate (litres/min)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple bubbler</td>
<td>10-100</td>
<td>1-30</td>
<td>general purpose: short contact between gas and liquid</td>
</tr>
<tr>
<td>Standard impinger</td>
<td>50-100</td>
<td>28 or less</td>
<td>useful for readily soluble gases and vapours</td>
</tr>
<tr>
<td>Midget impinger</td>
<td>10-25</td>
<td>2.8</td>
<td>useful for readily soluble gases and vapours</td>
</tr>
<tr>
<td>Scrubber with fritted-glass or other diffuser</td>
<td>25-100</td>
<td>0.5-20</td>
<td>good gas-liquid contact, but diffuser has a tendency to plug</td>
</tr>
<tr>
<td>Spiral scrubber</td>
<td>10-100</td>
<td>0.04-0.5</td>
<td>effective only at low flow rates</td>
</tr>
<tr>
<td>Packed tower</td>
<td>5-50</td>
<td>0.5-2.0</td>
<td>variable resistance; efficient only at low flow rates</td>
</tr>
<tr>
<td>Spray absorber</td>
<td>50-100</td>
<td>1-30</td>
<td>capacity of absorbent depends on design and size of absorber; useful for large-volume sampling</td>
</tr>
</tbody>
</table>

### 3.2.5 Factors Affecting Analytical Measurements

#### 3.2.5.1 Glassware

No chemical analysis can be accurate* or precise* unless it is conducted with calibrated glassware. This is not a great problem in these times, as the majority of laboratory glassware manufacturers produce measuring vessels guaranteed to conform to the standards prescribed by bodies such as the British Standards Institution, or the National Bureau of Standards. These standards prescribe such considerations as the capacity, temperature at which the unit is to be used, whether it is calibrated "to contain" or "to deliver", and the tolerance to which it has been made.

Volumetric flasks and measuring cylinders are calibrated "to contain", burettes and pipettes "to deliver". Volumetric flasks have a narrow neck, with one graduation etched on it to mark the volume of liquid which it is calibrated to contain. Having a narrow neck, it is possible to control the volume of liquid added more accurately than in measuring cylinders which are wider, and are generally only required to

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* These terms are defined in Section 5.1
3.3 Colorimetric Measurements

3.3.1 Photometric Analysis

Light consists of electro-magnetic radiation to which the human eye is sensitive, different wavelengths giving rise to different colours. "White" light is a mixture of all the wavelengths to which the eye responds. As an object absorbs a part of this spectrum of wavelengths, so it appears to be coloured, the colour depending on the wavelengths which are absorbed or reflected. Thus, a solution which appears blue does so because all wavelengths except those in the blue region are being absorbed.

These facts are the basis of the branch of science known as colorimetry. In this, the absorption of light by a solution of a coloured compound may be measured, and these measurements used to give information about its molecular structure or concentration in a solution.

The fundamental theory of colorimetric analysis is expressed in two laws,
Lambert's Law and Beer's Law. These laws state, in effect, that the percentage of incident light absorbed by a coloured material in solution is dependent on two factors. Firstly, the thickness of the absorbing layer (Lambert's Law). Secondly, the concentration of the coloured material in solution. (Beer's Law).

If the thickness of the absorbing layer is held constant, then the percentage of incident light absorbed is proportional to the concentration of the material in solution. In visual colorimetry natural or artificial white light is used as the light-source, and the colour intensity determined by visual comparison with solutions of known composition, or with coloured glass or gelatine discs of characteristics matching these solutions. If the eye is replaced by a photoelectric cell, the comparison may be made in numerical terms. The concentration of compounds which are themselves coloured, or which can be reacted chemically to produce a coloured compound can be determined in this way.

3.3.1.1 Colour Measurement or Comparison

The basic principle of most colorimetric measurements consists in comparing under well-defined conditions the colour produced by the substance in unknown amount with the same colour produced by a known amount of the material being determined. The quantitative comparison of these two solutions may, in general, be carried out visually or instrumentally.

In the visual method, the sample solution is made up to a definite volume, and the colour is compared with that of a series of standards prepared in a similar way. The comparison is made in suitable glass vessels, for example, colourless glass tubes of uniform cross section and flat bottoms, known as Nessler tubes. Equal volumes of standard solutions and the unknown are added to separate tubes and the colours compared by viewing vertically through the length of the tube, against a light background. In their absence, test tubes of matched diameter and wall thickness may be used. These are filled with the unknown and standards to the same height and again viewed vertically against a light surface. The concentration of the unknown is equal to that of the standard having the same colour. As a rule, it will be found that the colour intensity of the unknown lies between that of two successive standards. In such a case the concentration of the unknown is between that of the two standards and can be approximated if the concentrations in the two standards do not differ too widely. Usually it is best to first make a rough approximation of the concentration by taking standards of widely different concentration. Then a set of standards is prepared of which the extremes are slightly lighter and darker, respectively, than the unknown, and two successive standards found, one of which is slightly more and the other less intense than the unknown.

3.3.1.2 Instrumental Methods, Colorimeters and Spectrophotometers

Consider now the absorbance curve of a coloured solution, in this case, the solution which is measured in the determination of sulphur dioxide by the pararosaniline method. This is shown in Figure 15.
Figure 15 - Absorption Curve - Sulphur Dioxide, Pararosaniline method

Note that absorbance occurs between 450 nm and 650 nm, that is, the section of the spectrum between blue and orange. In terms of transmission, this means that the red and violet components of the spectrum are transmitted, and a purple solution results.

Optical density of such a solution may be measured using a colorimeter. This instrument is illustrated in Figure 16.

Figure 16 - Colorimeter

In its simplest design, it consists of the following essential parts:

(a) A light source, of suitable intensity, covering as large a wavelength as possible.

(b) A monochromator, which enables a section of the spectrum to be selected and projected through the solution under investigation.

(c) Cells to hold this solution. These must be transparent and chemically inert, and must only be used in carefully matched pairs, if the results are not to be distorted.
A detector to measure the intensity of the light transmitted through the solution under examination, and express it mathematically.

Amplifier and readout to record (d).

In practice, the section of the spectrum selected by the monochromator is at, or close to, the wavelength of maximum absorption of the solution to be measured, and is of as narrow a bandwidth as possible. In this way, the measurement is made with maximum sensitivity. The bandwidth is selected by inserting into the light beam a filter of the appropriate colour to isolate the desired spectral region. These filters may be of coloured gelatine or coloured glass, with the property of transmitting light in the specified region of the spectrum. This specified region will be in the region of the colour complementary to the colour of the solution under study. These are listed in the table below, Table 4.

Table 4 - Complementary Colours

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Colour Transmitted</th>
<th>Complementary</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-440</td>
<td>Violet</td>
<td>Yellow-Green</td>
</tr>
<tr>
<td>440-480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480-490</td>
<td>Green-Blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490-500</td>
<td>Blue-Green</td>
<td>Red</td>
</tr>
<tr>
<td>500-560</td>
<td>Green</td>
<td>Purple</td>
</tr>
<tr>
<td>560-580</td>
<td>Yellow-Green</td>
<td>Violet</td>
</tr>
<tr>
<td>580-595</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>595-610</td>
<td>Orange</td>
<td>Green-Blue</td>
</tr>
<tr>
<td>610-750</td>
<td>Red</td>
<td>Blue-Green</td>
</tr>
</tbody>
</table>

Filters of this type suffer the disadvantage that they have a wide spectrum bandwidth, usually of the order of 50 nm, hence lack the sensitivity obtainable when a narrow spectrum is used. Narrow bandwidth spectra can be obtained using a spectrophotometer. (Figure 17)

![Spectrophotometer Diagram](image)

This is undoubtedly the most accurate method for determining the concentration of substances in solution, when colorimetric methods are used, but the instruments are, of necessity, more expensive. A spectrophotometer may be regarded as a refined filter photoelectric photometer which permits the use of continuously variable and more nearly monochromatic bands of light. The essential parts of a spectrophotometer are: (i) a source of radiant energy; (ii) a monochromator, i.e. a device for isolating monochromatic light or, more accurately expressed, narrow bands of radiant energy from the light source; (iii) glass or silica cells for the solvent and for the solution under test; and (iv)
Concentration of the contaminant is determined by reading the length of the stain outside of the tube. They contain a reagent on a solid support (e.g., silica gel), capable of reacting with the compound under study to produce a coloured stain. The tube tips are broken off and a prescribed volume of air is drawn through, preferably using the squeeze bulb or piston type pump designated by the manufacturer. This ensures that air is drawn through the detector tube at the rate which gives the best results for that particular tube type. If an undesignated pump type is used, inaccurate results may be obtained. Concentration of the contaminant is determined by reading the length of the stain produced directly against the scale marked on the tube.

This technique should be used with caution, as some of the detector tube types available commercially are not particularly accurate, and, in some cases, the stain fades away at its leading edge, rather than having a clear, sharp limit. Under these conditions, it can be difficult to determine the exact length of the stain. Each tube type should therefore be checked against a standard gas mixture to determine its accuracy before use. Detector tubes have been primarily designed for use in industrial hygiene investigations, where higher concentrations of contaminant are usually experienced. Many are insufficiently sensitive to measure contaminant levels normally detected in ambient air, and this, too, must be determined before any tests are undertaken.

This does not apply to carbon monoxide detector tubes, which can be used to measure ambient concentrations above 5 parts per million. These are particularly useful in motor vehicle traffic surveys, for measuring instantaneous concentrations of carbon monoxide.
A typical detector tube and pump types are illustrated in Figure 18. It will be noted that in the case of the piston type pump, (Figure 18(b)), the piston handle may have graduations on it, so that a volume of air less than the volume of the barrel may be readily drawn through the detector tube. Manufacturers directions concerning checking the pump for leaks and checking flowrate through the detector tube should be carefully followed. Care should be taken to ensure that gas flow through the tube is in the direction indicated by the arrow marked on the inlet end of the tube.

Figure 18(b) - Piston Pump and Detector
The average concentration of a pollutant over a longer period of time (say, one hour or more) may be determined by using the simple apparatus illustrated in Figure 19. The detector tube is inserted in a two holed stopper in a large, water-filled bottle. A siphon tube is inserted through the other hole. Flowrate of the siphon is controlled by a screw clip, so that the bottle empties over the period of time desired. The volume of air sampled is thus equal to the volume of water siphoned out. Mean concentration of pollutant in the air is calculated from:

\[
Co = \frac{C_m \cdot V_p \cdot n}{V_s}
\]

Where:
- \(Co\) = Mean concentration of pollutant in air
- \(C_m\) = Concentration as measured by tube
- \(V_p\) = Volume sampled by one stroke of pump, as specified by the tube manufacturer
- \(n\) = Number of strokes of pump specified by the manufacturer for normal reading of the stain
- \(V_s\) = Total air volume sampled

3.3.3 Calibration Graphs and their Preparation

In any colorimetric technique an accurate calibration graph is vital. Without it, the whole analysis is worthless. Such a graph is prepared by analyzing a number of standard samples, each containing a known concentration of the pollutant under analysis, these concentrations covering the total range over which Beer's Law holds. From these, a graph of concentration against optical density is drawn. (Detector tubes do not require calibration of this type since they carry their own calibration, marked on the side of the tube.)

The standards may be prepared either as "synthetic standards" or by the analysis of prepared gas mixtures, containing a known concentration of pollutant. The first of these techniques is used in the determination of sulphur dioxide, as described in Chapter 2, Section 2.2.1, of "Selected Methods of Measuring Air Pollutants", page 38. In this, a solution of sodium sulphite is prepared, and standardised, using a classical wet chemical technique. This is diluted into a
potassium tetrachloromercurate solution to provide what is, in effect, a stabilized solution of sulphur dioxide, in the concentration range of micrograms per c.c. This solution is further diluted to provide the standards required. It must be established (usually empirically) that a relationship exists between gas concentration and concentration of salt in the standardising solution. This is illustrated in Chapter 4, Section 4.4.2.4, page 73, analysis of nitrogen dioxide by the Saltzmann method. Here it states, "It has been determined empirically that 0.74 mole of NaN₂ produces the same colour as 1 mole of NO₂". The accuracy of the method depends on the volatility of that factor 0.74.

Calibrated gas mixtures may be prepared in several ways. Broadly, they are classified into static or dynamic techniques. In the static techniques, a known amount of pollutant is introduced into a known volume of pollutant free air. If the pollutant is liquid at ambient temperatures, it may be introduced using a microsyringe, if gaseous, a gas tight syringe may be used. The pollutant may be introduced into a rigid, semi-rigid, or flexible container, where it is mixed with a known volume of air. This mixing may be encouraged by including in the container strips of glass, aluminium or teflon, and shaking the container vigorously. Mixing in a flexible container may also be attained by only partly filling it and vigorously kneading it after the pollutant has been added. The task is made easier if the pollutant is added to the air stream as the bag fills.

Again, it must be established that there is no loss of pollutant by adsorption or diffusion, before mixtures prepared in this way can be regarded as primary standards.

In the preparation of standard gas mixtures by dynamic techniques, known flowrates of pollutant and pollutant free air are mixed together to produce the desired concentration. In its simplest form, this is done using compressed gases or pumps and flowmeters. It is not practicable to produce concentrations in the low parts per million range in this way, the flowrate of pollutant required is too small to be measured accurately. Instead, a mixture containing several hundred parts per million of pollutant is first generated, and this is further diluted in a second stage of the system.

Permeation tubes provide a means by which small known amounts of a gas may be accurately metered into an air stream. These were developed by O'Keefe and Ortmann, who noted that many gases would diffuse through a plastic membrane at very slow rates, rates of nanograms (10⁻⁹ gram) per minute. FEP Teflon tubing was found to be a suitable means of storing and handling liquified pollutants, while providing permeation rates which allowed gas mixtures to be produced in the concentration range required, using realistic flowrates of dilution air. The permeation rates noted by O'Keefe and Ortmann are shown in Figure 20.8

Figure 20 - Permeation Tube Data
Note that the permeation rates shown are highly temperature dependent, hence the tubes must be kept at a strictly controlled temperature when in use, preferably better than ± 0.1°C. Techniques for achieving this are shown in Figure 21; also in Figures 2-3 and 2-4 of "Selected Methods of Measuring Air Pollutants". Later, commercially produced, permeation tubes are less temperature dependent (Figure 20) obviating the need for complex temperature control systems, however, control to better than ± 0.5°C is still required.

Permeation tubes should be calibrated by weighing, then holding the tube at controlled temperature for several days with air flowing over it, and reweighing. After establishing four or five weight-against-time readings these should be graphed, and from this the permeation rate, in nanograms per minute, calculated. Scaringelli, O'Keefe, Rosenberg and Bell have given detailed, explicit directions for permeation tube calibration, and their paper should be studied before any "home" calibration is attempted.

It is important to pass air through the system for several days at the calibration temperature to condition the permeation tube before any weighing programme is commenced.

Properly calibrated permeation tubes may be regarded as primary standards for gas analyses in this range of concentrations. It is only by the use of controlled gas mixtures that the collector efficiency can be checked.

Several commercial manufacturers in the United States produce calibrated permeation tubes, along with a certificate of calibration, traceable to a National Bureau of Standards calibration.

Figure 21 - Permeation Tube Calibration Systems

Figure 21(b) - Permeation Tube Calibration Systems
4. SAMPLING AND MEASUREMENT - PARTICULATE MATTER

This subject is covered in Chapter I of the publication "Selected Methods of Measuring Air Pollutants"; and these notes may be regarded as supplementary to this Chapter.

Solid particulate pollutants may be arbitrarily defined and classified as follows:

**Dust Fallout:** Solid material, such as grit, coarse enough to settle out of the air fairly rapidly.

**Suspended Particulate Material:** Material of particle size less than 100 microns. This is chiefly as "nuisance dust", which is capable of being airborne for a long enough period to be carried into homes or other buildings and deposited on clean surfaces.

**Smoke:** Smaller particle size material, of less than about 10 microns, mainly comprised of unburnt carbonaceous material, derived from fuel burning sources. This material lies within the range of respirable particle sizes, and consequently can pose a possible health risk.

4.1 Particulate Filter Materials

Whenever suspended particulate matter is to be collected by filtration, or whenever a particulate filter is installed to protect a sampling train, due consideration must be given to the composition of the filter medium.

Materials most frequently used in filter manufacture include cellulose, cellulose esters, glass fibres and synthetic polymers.

Cellulose filters are often used in routine air monitoring, particularly where the collected material is to be measured by reflectance or transmission densitometry. They have a low ash content, which is a distinct advantage where later analysis of the collected material involves ashing the filter. However, they offer too great a resistance to air flow to be useful in high volume sampling.

Glass fibre filters offer considerably less restriction to air flow, and are to be preferred in high volume sampling. However, they are far more fragile than cellulose filters, which limits their usefulness. Being brittle, they cannot be folded before use, as the glass fibres along the fold will fracture, ruining the filter for use in a high volume sampler. Analytical balances to be used in weighing high volume sampler filters must therefore have a weighing chamber large enough to accommodate a 20 cm x 25 cm filter, unfolded. They also suffer the disadvantage that the filters usually obtainable have a high trace metal level in the fibres. For this reason, the collected particulate matter cannot be analysed for trace metals by techniques which do not involve solution of the metal from the filter. For example, X-Ray fluorescence, which analyses the material directly on the paper, cannot be used unless a higher grade of filter, containing a low level of trace metals, is used.  

Membrane filters may be prepared from a cellulose ester, with the pore size controlled to fine limits during manufacture. They can be used to trap particles down to 0.1 micrometres in diameter, but again suffer the disadvantage of a high flow resistance, particularly when the pore size is small. A porous backing plate or fine mesh screen must be used as a support, since the filter itself is quite thin and brittle.

Nucleopore filters are made by irradiating a thin polycarbonate sheet with neutrons, etching pores of constant dimensions. They are similar to membrane filters in many respects, particularly in the need for a backing support. Both of these filter types have a low ash content, and low levels of background impurities. They are thus ideally suited for analytical work using more sophisticated techniques.
4.2 Suspended Particulate Matter

Several methods are available for measuring suspended particulate concentrations. The most widely accepted, the United States EPA High Volume ("Hi-vol") sampler, is dealt with in detail in Chapter 1 of "Selected Methods of Measuring Air Pollutants". An additional method, the OECD Gravimetric Method and the OECD Filter Soiling Method are also covered in this chapter.9 The OECD Filter Soiling Method has been modified, and published in British Standard 1747, Part 2, 1964.10

4.2.1 Selected Particle Size Samplers (Dichotomous Samplers)

If the results of suspended particulate monitoring are to be correlated with health effects studies, a range of smaller particle sizes must be considered, since only those particulates which enter the body will contribute to the health effect. This involves the sampling and fractionation of particles of less than 15 micrometres in diameter, since it has been established that only particles of less than this diameter enter the lower respiratory system during mouth breathing and less than 2.5 micrometres during nose breathing.

Subdividing particulates into these size ranges may be accomplished by the technique of Cascade Impaction.

When an airstream is deflected around an object, or constrained to move along a curved path, particles are thrown out of the streamlines by inertia, that is, by their tendency to keep going straight when the fluid flow turns a corner. The particle, which leaves its original streamline and moves across other streamlines, may ultimately strike the deflecting object. This phenomenon is generally called impaction, and the particles may stick to the surface on which they impact if the particle is small enough and if the velocity is not too high.

Whether or not a particle leaves the airstream is a function of the size and mass of the particle and the velocity of the airstream. The higher the velocity, the smaller the particle which will leave the stream. Thus, if an airstream is caused to flow through a slot, then to turn at right angles, particles can be caused to impact on a surface immediately in front of the slot. If the airstream velocity through the succeeding slot is increased (by decreasing the width of the slot), then smaller particles will impact in that stage. Succeeding stages may be added to cause the impaction of smaller and smaller particles. If the volume flow through the unit is carefully controlled, then the cutoff point for each stage may be accurately predicted.

![Figure 22 - The Cascade Impactor](image_url)

The equipment to achieve this (the Cascade Impactor) is illustrated in Figure 22. Suspended particulates enter the impactor through parallel slots in the first impactor stage, and particles larger than the cutoff size of the first stage impact on the collection paper opposite the slot. The airflow then passes through slots in the collection substrate, accelerating through the narrower slots of the second impactor stage, where particles greater than the particle...
cutoff size of the second stage impact on the second collection paper, and so on. The collection papers are weighed, before and after use, and the results reported as weight of material collected in the specific size ranges, using the size ranges predicted by the manufacturer.

4.3 Smoke

4.3.1 OECD Filter Soiling Method

The stain resulting from sampling by this method is comprised of a heterogeneous mixture of dust, combustion products and industrial emissions. The composition will vary from time to time and from place to place, hence the darkness of the stain will not be proportional to the total mass of suspended matter in the air volume sampled. It is simply an indication of the suspended material in the air, in most cases, the products of combustion.

The suspended material being sampled is heterogeneous in origin and composition, and subject to continuous variation, so that any calibration curve of concentration against stain darkness can be valid only for one particular place at one particular time. This applies equally to calibrations derived from transmission densitometry and calibrations derived from reflectance densitometry. However, it has been established experimentally that the shape of the calibration curve, although it varies, does not vary beyond reasonable limits. The method of establishing the scale and shape of the calibration curve, to give the possibility of a workable index of dark smoke from a reflectometric reading is recounted in Chapter 1 of "Selected Methods of Measuring Air Pollutants".

Experimental data have indicated that for a wide variety of smokes a satisfactory calibration curve may be constructed, which is sufficient to correlate darkness index and surface concentration, if the latter is expressed in terms of a "Standard Smoke". It must be recognised that an inherently indefinite quality, referred to as "dark suspended matter" or "smoke" is being measured. If the results of the measurement are not exact, or if the calibration appears arbitrary, these are a necessary result of the variability of the material being measured. The more precisely a particular component of the pollution is defined, the more exact will it be possible to make its measurement, but the less universal may be the value of the result.

4.3.2 ASTM Method, D1704-61

This method described a technique which is basically the same as the OECD method, using an automated sampling instrument to collect the samples. (Figure 23).

However, this method does not report results as a weight/volume ratio, but in terms of arbitrary units, Coh (Coefficient of Haze) units, Km units or Ruds (Reflectance Unit of Dirt Shade).

The method of calculating these, as set out in the ASTM Method, is quoted below:

Calculation

(a) For comparison purposes with similar samples collected in other sampling areas and under sampling conditions where the area of paper exposed and the volume flow rate may be different, the optical density values for transmission are converted to a unit scale called the Coh unit. The Coh unit is defined as 100 times the optical density of the deposit, so that an optical density of 0.301 is 30.1 Coh units. Furthermore, since the intensity of the filter paper stain is determined by the total volume of air aspirated through the filter and the area of the exposed filter, the size of the air sample is properly expressed in linear units of air, that is, the volume of air aspirated divided by the
area of the filter. For convenience, the results are reduced to multiples of 1000 lin.ft. of air sample, so that the soiling for any time period is described in terms of Coh units per 1000 lin.ft. of air.

![Diagram of AISI Automatic Smoke Sampler]

**Figure 23 - AISI Automatic Smoke Sampler - Diagramatic**

(b) If the quantity of air sampled during each spot sample is equal to L, in thousands of linear feet, then:

\[
L = \frac{\text{flow (cu.ft. per min.)} \times \text{sampling time in min.}}{1000 \times \text{circular area of spot (sq. ft.)}}
\]

Cohs per 1000 ft. = \( \frac{\text{optical density} \times 100}{L} \)

**Example:** Suppose measurements with the gas flow meter have established the average flow rate through each spot area of paper as 0.22 cu.ft. per min., the area exposed is a sampling circle 1 in. in diameter or \( 5.45 \times 10^{-3} \) sq.ft., and the timing spindles of the instrument are set for 2-hr samples, then:

\[
L = \frac{0.22 \times 120}{1000 \times 5.45 \times 10^{-3}} = 4.85 \text{ (thousands of feet)}
\]

If a given spot shows a light transmission value of 50 percent, then:

\[
\text{Optical density} = \log \frac{100}{50} = \log 2 = 0.301
\]

Cohs per 1000 ft. = \( \frac{0.301 \times 100}{4.85} = 6.2 \)

4.3.3 **Dustfall**

This is measured by locating an open topped collector on a suitable stand in the area to be studied. Collector design and specifications vary widely from country to country. The ASTM Standard D-1739 calls for an open cylinder of vertical sides and a flat bottom having prescribed dimensions of size, height and diameter, mounted in a suitable holder (Figure 24(a)). Similar types of collector have been prescribed in other parts of the world, e.g. in the Federal
Republic of Germany, where a household preserving jar of 1.5 litre capacity on a suitable stand has been adopted. The British Standard (B.S. 1747, Part 1) prescribes a much more complex assembly, comprising a stand, complete with birdguard, and a collecting bowl of standard proportions (Fig. 24,b)). The Australian practice is simpler than this. It calls for a glass funnel 15 cm diameter to be set in the neck of a 4.5 litre glass bottle, held in a metal can on top of a simple pipe stand. (Figure 24,c)).

Water, to entrain the dustfall and an algicide, to prevent the growth of algae in the collected water, are usually added. The collector is normally left out for a period of one month, after which time it is returned to the laboratory, and the following parameters determined, after screening out leaves, twigs, insects and other non-dustfall materials:

(a) Quantity of liquid collected and its pH
(b) Total weight of dried, insoluble material
(c) The weight of ash obtained by combustion of the insoluble material
(a) Weight of soluble material dissolved in the water.

Chemical analysis of the soluble and insoluble material may also be performed.

Dustfall measurements are commonly used to indicate the readily settleable portion of particulate air pollution. Typical values for a city are:

Residential: 65-130 milligrams/metre$^2$/day (5-10 tons/mile$^2$/month)
Light Industrial: 100-200 milligrams/metre$^2$/day (7.5-15 tons/mile$^2$/month)
Heavy Industrial: 150-350 milligrams/metre$^2$/day (11-26 tons/mile$^2$/month)

High values of 2,600 milligrams/metre$^2$/day (200 tons/mile$^2$/month) have been recorded close to uncontrolled sources. This method of sampling is quite inaccurate, but it does give an indication of overall dirtiness of an area, and is useful in determining trends.

---

Figure 24: Dustfall Gauges
5. VALIDATION AND PROCESSING OF DATA AND REPORTING OF RESULTS

One of the main objectives of the WHO air monitoring project is to standardize the method of handling and reporting air pollution data. Taken in conjunction with the promotion of uniform methods of measurement this programme will help in generating internationally comparable data on levels and trends in air pollution.

The coding structure and method of entering information on data forms to allow for computer processing and subsequent statistical analysis of the data is described in Chapter 6 of WHO Offset Publication No. 24 "Selected Methods of Measuring Air Pollutants", World Health Organization, Geneva (1976), pp 95-112.

5.1 Accuracy, Precision and Validity of the Data

A clear distinction should be made between the terms "precision" and "accuracy" when applied to analytical methods. Precision is a measure of the reproducibility of a method, regardless of whether observed values are widely displaced from the true value as a result of systematic or constant errors. Accuracy on the other hand, is a measure of the absolute error of a method and may be expressed as a comparison of the amount of a substance measured by the test method and the true amount present.

It is perhaps axiomatic that the validity of any reported data value is dependent upon the accuracy and precision of the measurement. In turn, the accuracy and precision of the raw data depends upon the sampling and analytical method used and the capability of the person performing the sampling and analysis. Special attention should be taken to validate any extreme values observed because they, more than other values, are apt to influence the summary statistics. Any instrument must of course be in calibration and in proper operating condition.

Considerable care must be taken in the reporting of results in the data forms as the use of inaccurate or incorrectly entered data will affect the statistical summaries obtained from each monitoring site.

It is meaningless and confusing to report a degree of precision outside the limits of sensitivity of the analytical procedures. For example, reporting a value of say 182.5 g/m³ would imply (i) that such precision is possible and (ii) that it makes a real difference whether the value is 182 or 183 g/m³.

Individual measurements of air quality can be considered to be members of a population of values which characterize the particular pollutant and measuring site. It is useful to derive statistics which summarize the data which has been selected in some way from the total population. Depending upon whether the sample can be considered to be statistically representative, it may or may not provide data that can be used to make inferences extending to the entire population.

A very useful method of data presentation is to group the data into intervals and to count the number of data values that fall within each interval. Such a frequency distribution may be described by summary statistics which measure the central tendency of the distribution. If the frequency distribution is nearly symmetrical, then the data can be described by a normal distribution, and the most appropriate parameter to summarize the data is the arithmetic mean. This is simply the sum of the individual values divided by the number of values. In addition to the measure which is most representative of the data (in this case the mean), it is necessary to have an indication of the spread of the observations. Standard deviation (\( \sigma \)) is the most commonly used measure of variability. This subject is covered in detail in WHO Offset Publication No. 51 "Analysing and Interpreting Air Monitoring Data".
decrease in the daily minimum concentration over a period of several days may indicate a decrease in the daily minimum concentration over a period of several days may indicate

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Air Monitoring Data

monitoring data are referred to the WHO Offset Publication "Analysing and Interpreting Air Monitoring Data".

result of measurement error, analytical error, recording error or transcription error. result of measurement error, analytical error, recording error or transcription error.

The data should be representative and it is important that the samples be collected with equal frequency during periods where variations due to seasonal trends may be evident. For example, if winter sulphur dioxide readings tend to be much higher than summer values, it would not be logical to obtain a yearly arithmetical average based on predominantly winter or predominantly summer values. In such a case, it would be necessary to weight these seasons (together with values obtained in the Spring and Autumn) evenly to obtain the Annual Mean and related statistical summaries.

Readers seeking a comprehensive guide to the statistical analysis of air monitoring data are referred to the WHO Offset Publication "Analysing and Interpreting Air Monitoring Data".

The purpose of data validation is to detect and then correct any data values that may not represent actual air quality at the sampling station. Such values may be the result of measurement error, analytical error, recording error or transcription error. In general, it is not possible to validate each individual value recorded. Instead, attention is paid to those results which will influence significantly the summary statistics.

Review of all data tabulations by an experienced worker is a powerful validation tool. Alternatively, it may be possible to present such data graphically. The purpose of this inspection is to locate unusually high or low values that might indicate a gross error in the data generation system. It is, however, not sensitive to intermediate values that can be in error and significantly influence the summary statistics. A second purpose served by manual data inspection is the detection of uncorrected drift in the calibration of a continuously measuring instrument. Observation of an increase or decrease in the daily minimum concentration over a period of several days may indicate that the instrument suffers from a zero drift problem which may indicate a faulty instrument or faulty calibration equipment.

In an automated data processing system, procedures for data validation should be incorporated into the basic programme. Routines to check for extreme values are easily implemented. In addition, all values can be examined by comparison with immediately preceding and following values to check for unexpected patterns, given a knowledge of both instrument response time and sampling interval.
5.2 Quality Control and Quality Assurance of Air Monitoring Samples

A detailed account of quality control and quality assurance is contained in the United States Environmental Protection Agency three volume publication "Quality Assurance Handbook for Air Pollution Systems" under the titles "Principles" (EPA 600/9-76-005),15 "Ambient Air Specific Methods"; EPA 600/4-77-027a16 and "Stationary Source Specific Methods" (EPA 600/4-77-027b).17 Those requiring to develop a full control and assurance programme should consult these volumes.

The distinction between quality control and quality assurance should be clearly understood. Quality control concerns itself with the quality of a product, in the case of an air monitoring programme, the data being generated. Quality assurance concerns itself with assuring that the quality control system is performing adequately.

In air monitoring studies, quality control is chiefly an internal function, in that it is concerned with routine checks to be included in normal internal procedures. These include routine calibrations, duplicate samples, split samples and "spiked" samples, that is, samples in which a known amount of pollutant is added to an already collected sample.

Quality control is concerned in all aspects of air quality data generation, from best siting of the monitoring station, through sample collection, sample analysis, data processing and including the analyst or operator performing the task.

Quality assurance is a function external to these, normally conducted by someone external to the routine data collecting and processing programme. However, the organizations policy on quality assurance, and the manner in which this policy is implemented should be clearly understood by all persons involved in the monitoring programme. The quality assurance objectives should be written down, and readily available to all personnel concerned. Attainment of these objectives will lead to the generation of data of acceptable quality, at the minimum cost consistent with this quality. Acceptable data must conform to all requirements, in terms of completeness, precision, accuracy, representativeness and comparability.

Complete, if the prescribed percentage of total possible measurements is present.

Precise and accurate, if they conform to the prescribed standards for data quality.

Representative, if they present a true picture of the condition being measured. For example, peak hour readings must be taken at peak hours, and these must not be taken to represent average conditions for the day.

Comparable with data from other sources, if they are in consistent units, corrected to the same temperature and pressure.

5.2.1 Sample Collection

Although quality control and quality assurance may be regarded as separate functions, they are in many cases interconnected. For example, there are routine quality control checks which must be performed during sample collection. The inlet sample line should be checked regularly for leaks or for the accumulation of dust, insects or spider webs in the line. Where flow rate or volume measurements are involved, the accuracy of the measuring device should be checked. Where a bubbler sampling method is used, the volume of absorbing
liquid must be adequate, both in terms of volume and concentration of reagent.
Continuously recording instruments should be regularly calibrated, either by the
use of a calibrated span gas, or by a suitable electronic method. In each case,
there is a quality assurance aspect to be considered as well. This may be a
simple matter, for example, it may only involve recording in a log book that the
check has been performed and the result of the check. The result of the check
is of importance, since it is through this that the reliability of the particular
method and instrument may be determined. The span gas used to calibrate a
continuously recording instrument should itself be thoroughly checked,
preferably by comparison with a primary standard or with another standard
traceable to National Bureau of Standards, or a similar standards organization.
These are simple quality assurance exercises; at the other end of the scale,
detailed statistical analysis of the data generated might be involved.

5.2.2 Sample Stability and Analysis

The quality of any analytical result will depend, amongst other things,
on the sample and the reliability of the analytical method and equipment. These
two factors need to be checked from time to time.

Sample stability may be simply checked by analysing aliquots of a sample
over a period of time equivalent to the length of time which the sample will be
held before analysis. Similar control checks should be used on the analytical
procedure. These include the use of sample blanks to establish zero readings,
analysis of aliquots or duplicate samples to establish repeatability and
reproducibility of the method, and the use of spiked samples to establish the
percentage sample recovery during extraction or reaction steps in the analysis.

Intermittent control checks to be performed include the use of sample
aliquots to determine precision, and standard reference materials or samples
to determine accuracy and precision.

The quality assurance function in this case includes analysis of the
records of the above quality control studies, and inter-laboratory trials, using
standard reference samples.

Interlaboratory trials will serve to identify those laboratories that are
biased, and to estimate the reproducibility of results between laboratories.
Factors influencing interlaboratory testing include:

- unbiased treatment of reference samples by the participating analyst,
  if it is apparent that the sample is a reference sample and not a
  routine sample.
- stability of the reference sample during storage and shipping.
- proper interpretation of the test procedure by the participating
  laboratories.

It must be emphasised that in all these studies, it is not the integrity
of the operator or the laboratory that is under trial. We are seeking to
establish that the participating laboratories are carrying out a well defined,
well tested method properly. If the results are unsatisfactory, the reason must
be established, for example, because of faulty procedures or faulty chemicals.
In other words, it must be demonstrated that the method is reliable (through
inter-laboratory testing) and, secondly, that this tested method is being
properly used by the different laboratories.
6. DESIGN OF THE MONITORING PROGRAMME

WHO Offset Publication No. 33 "Air Monitoring Programme Design for Urban and Industrial Areas" examines inter alia monitoring objectives and approaches, network design, station location criteria and other essential components of the monitoring programme.

The following notes are intended merely to supplement this material.

6.1 Purpose of Sampling

Before deciding upon the number and location of sampling sites, it is necessary to clearly establish the objectives of the sampling. Although it may be tempting to design a system that could satisfy a considerable number of different objectives and data needs, in practice this is rarely possible. The most usual objective is the general evaluation of air quality and this includes the gathering of historical data to observe long-term trends as well as data to evaluate compliance with air quality standards and to evaluate control strategies.

Other possible objectives are:

- Evaluation of episode-type pollution and (sometimes) activation of emergency control procedures.
- Assessment of risks to human health and the environment generally.
- Validation of air dispersion models.
- Assessment of source-oriented data to investigate the contribution from specific sources of pollution.
- Provision of data for initial assessment surveys and to provide a basis for land-use planning.

Often these objectives or purposes are inter-related but should not be confused in considering the site of an instrument or sample intake.

6.2 Number and Location of Sampling Sites

This subject is covered in depth in WHO Offset Publication No. 33, "Air Monitoring Programme Design for Urban and Industrial Areas".1

Only general guidelines can be given for estimating the number of stations needed for the required assessment of air quality. The determining factors usually include the types of data needed, population and size of the area, spatial distribution of industry, resources available and topographical and meteorological factors. Although grid patterns have been used to define measuring locations on a number of occasions in the past, they tend to be wasteful of staff time and resources.

Today more emphasis is placed on site locations based on delineation of pollution variability throughout the area. As a consequence, the majority of stations are placed in the more heavily polluted areas and also in areas of highest population densities. Topography plays an important part in the selection of possible monitoring sites because of its effect on local wind patterns. In this connection, contour maps can provide an extremely useful input. Population density maps, past air quality data and emission source information are also useful when site location decisions are to be made.

Although ideally the placement of monitoring instruments for each pollutant should be based on the geographic distribution of that pollutant, it is likely that this could require a separate network of stations for each pollutant. Except for secondary pollutants produced by photochemical reactions in the air, and high concentrations of carbon monoxide and lead, which may require specific sites related to the source of the emissions, it is usually possible to develop a single network to monitor all pollutants of interest.
From a practical viewpoint, the most important criteria in locating a sampling site in many communities are often security from vandalism and the availability of suitable buildings.

In episode-type studies the averaging time must be sufficiently short to permit characterization of the episode (i.e. continuous recordings or three-minute means would for this purpose be far more appropriate than 24 hour integrated results). As the results should be indicative of the "worst" conditions, the sensors are usually placed in the plume line of the emission sources. Otherwise much the same considerations apply as for long-term historical monitoring.

Source oriented sites are far more limited in scope, but seek to identify the contribution from a single source or group of sources. Sufficient sites should be chosen to delineate between different sources in the same general downwind direction. At least one site should be chosen such that based on wind direction data, the contribution from the sources under study would be expected to be minimized.

6.3 Criteria for Siting

There are difficulties in establishing firm criteria for siting air monitoring stations in urban areas largely because each site has unique characteristics. However, a WHO Conference on Trends and Levels of Air Pollution\textsuperscript{16} did reach agreement on general criteria. It was considered that the following points must be considered:

A. Monitoring stations for mobile sources:

1. Traffic density and the distance to the nearest traffic lights.
2. The sample intake - not closer than 1.5 m or more than 30 m from the traffic, not more than 4-5 m above ground, not less than 1 m above ground, and not closer than 1 m to the nearest wall.
3. Meteorological conditions such as prevailing wind and dispersion.
4. The height of the surrounding buildings (not to exceed an angle of 30\textdegree{} above the horizontal).
5. The likelihood of new constructions which may affect a selected site.
6. Established monitoring stations should not be moved unless absolutely necessary.

B. Monitoring stations for pollution from stationary sources:

1. The site must be located in a populated area.
2. Several sites must be located downwind of the effluents.
3. The sample intake must be exposed to the pollutants in an open area.

In some cases, it may be possible to combine categories A and B at one sampling site.

Monitoring Sites for Secondary Pollutants present special problems. To detect maximum average concentrations, it is necessary to locate the sites sufficiently far downwind from the major sources of generation of precursor pollutants so that the concentrations can be determined at the time when these maximum concentrations occur. For example, when monitoring for ozone, the time delay is usually 1½ to 2 hours after the occurrence of the major morning peak hour. This often means that sites for the measurement of secondary pollutants are located 8-12 km from the major downtown traffic sources. However traffic patterns and meteorological considerations are important here and a good deal of preliminary surveying may be necessary, especially in large cities in hot climates, to establish the duration of the time delay and together with the meso and micro-climatological considerations, the best location for these sites.
6.4 Sampling Frequency and Duration

Three types of sampling are normally used in studies of air pollution, namely short-period or "spot" sampling, batch type sampling of longer duration (usually for 24 hours) and continuous sampling for the evaluation of peak and average concentrations over definite time-intervals.

Spot samples are usually collected over periods varying from less than 30 minutes to several hours for specific, well-defined purposes. Such samples have only limited value except where traffic or other local sources of pollution cause only minor changes in concentration at particular periods of the day. Spot sampling is also useful for the random checking of pollution at many points. Because pollution levels generally fluctuate widely depending upon meteorological conditions, topographical features and various factors associated with the sources of pollution spot sampling cannot give a comprehensive picture of the nature and magnitude of an air pollution problem.

Continuous sampling techniques by means of properly calibrated automatic instruments are usually necessary in systematic studies of the nature and extent of air pollution, especially if the data is to be of value for epidemiological surveys and for episode-type monitoring. However, continuous sampling instruments may at times lack specificity and data obtained from them must be checked by comparison with data from other more specific analytical methods.

Batch sampling may be carried out by the chemical absorption or filtration of measured air volumes sequentially in time. Samples of 1-, 2- or 3 hours duration are commonly used for smoke stain determinations. Sequential bubblers are usually used on a 24 hour basis. Although instantaneous peak values cannot be obtained, these samples nevertheless enable a continuous record of pollution levels using a fixed averaging period to be obtained. Such records are limited in their usefulness by the duration of the time period involved.

Because of the large seasonal variation in concentration of some pollutants representative seasonal periods of each year should be included. Several years' consecutive data will be needed to avoid drawing hasty conclusions - apparent trends may be due to variations in weather patterns, etc.

The choice of sampling period is at times dictated by diurnal or other cyclic events. An example is the concentrations of oxides of nitrogen which are dependent inter alia upon morning and afternoon traffic peaks. Alternatively, the choice of the sampling period may depend upon the nature of the compound under study and its stability to oxidation, light or other factors.

The duration of sampling is also influenced by the concentration of the pollutant (a constraint at times being the amount of material needed to obtain an assay) and by the sensitivity, accuracy and precision of the analytical methods to be used. Frequent short-term sampling is often more advantageous than cumulative sampling, since the latter can still be obtained by summation of the results of a series of short-period samples.

6.5 Installation of Instruments

The dimensions of the high-volume sampler are given on pages 5 and 6 of WHO Offset Publication No. 24, "Selected Methods of Measuring Air Pollutants". It is important that the sampler is located a sufficient height above ground level to avoid entrainment of ground level dust. For this reason, High Volume Samplers are often placed on awnings or the rooftops of one-storey buildings.

Intermittent and continuous gas monitors are housed inside a shelter to protect them from rain, wind and vandals, with a sampling probe projecting about one metre above the roof. To avoid the ingress of rain, the inlet to the sampling tube is protected by a small funnel opening downwards. All sampling equipment must be readily accessible to permit normal operation and maintenance, yet secure from vandals. It is good practice to place the sampling equipment away from office and living areas so that noise emanating from the devices does not cause a nuisance.
Most continuously-recording instruments are designed to operate at temperatures below 350°C. Consequently, in hot climates air conditioning of the monitoring station may need to be considered.

6.6 Support Activities

The successful operation of a monitoring network itself requires a number of support activities. The most important of these are:

(i) Initial check and calibration of monitoring instruments.
(ii) Routine calibration.
(iii) Supplies and maintenance.
(iv) Quality control.
(v) Training.

Before deployment at the sampling sites, all monitoring instruments must be checked for operational reliability and calibrated, and also tested for proper air and reagent flow rates, for possible leaks in the various reagent flow systems and for proper functioning of all mechanical systems. The need for careful pre-evaluation cannot be over-emphasized. Many operational problems may be uncovered and corrected through this type of evaluation.

After each monitoring instrument is operational, calibration checks must be scheduled and performed routinely to ensure the continuity of valid data. The use of both static and dynamic calibrations is recommended. Static calibration is used to check the response of the sensor. This involves the use of standardized solutions containing a known amount of the pollutant or in the case of calorimetric type instrument of filters which influence the response of the detector to some predetermined value.

Dynamic calibration involves calibration with a known concentration of gaseous pollutant while the system is operational in the field. The operator must use a method that delivers a known concentration to the system. For example, for total hydrocarbon and carbon monoxide instruments, standard gases with certificated analysis are available commercially; for sulphur dioxide and nitrogen dioxide monitors gravimetrically calibrated permeation tubes can be used to generate air streams of known pollutant concentration. No comparable calibration method exists for hi-vol samplers and careful calibration of the air flow metering device is required.

Before any monitor is selected for routine field use, it is important to investigate the availability of replacement parts and required accessories. This is a fairly critical consideration, yet is often overlooked. In addition, calibration and support gases of appropriate purity must be available on a continuing basis. Proper storage must be provided for unstable and toxic materials.

The proper use of quality control techniques will assure the validity of monitoring data.

Operators may be trained either before or after the monitoring equipment is installed at the stations. Each operator should be instructed in field operation of the monitoring equipment before data are accepted. Specific training might include:

- monitoring equipment theory
- recording of the instrument operational parameters - flow rate, calibration checks, reagent indicator levels
- routine maintenance
- sample-handling procedures
- simple field repairs

It is important that each operator understands handling of the collected intermittent samples. Ordinarily, Hi-vol particulate samples can be stored in envelopes at room temperature indefinitely and returned to the laboratory for analysis at a later date. Data such as date, air volume, etc., should be recorded on the envelope. Bubbler solutions, however, should be analysed as soon as possible after the sample is collected.
7. **MAINTENANCE AND REPAIR OF MONITORING EQUIPMENT**

The development of maintenance schedules and the repair of equipment is largely a matter of systematic thinking and organised common sense.

### 7.1 Maintenance Programme

Maintenance schedules should be regular, at time intervals dictated by experience of the instrument. Consider the High Volume sampler as an example. Here there are two maintenance functions, as distinct from calibration, which is another function to be performed regularly. The inside of the sampler cabinet should be regularly cleaned to remove dust which has collected in it, particularly in the area under the gable roof near the filter holder. In this case, "regularly" means each time the unit is serviced, after the used filter is removed, and before the clean filter is inserted. The motor brushes should be regularly checked, and replaced when necessary. In this case, "regularly" need not mean each time the unit is serviced, experience may show that the brush life is measured in months rather than days, so checks can be made every third or fourth service. It is vital, however that the frequency of checking should be such that deterioration in any part of a unit is detected well before a breakdown occurs, and the unit suffers damage.

The equipment used to monitor sulphur dioxide by the pararosaniline method requires a similar type of maintenance scheduling. Items which require regular checking include air pump function and cleanliness of bubblers, filters and sample lines. If a gas meter is used to record sample volume, it should be removed and recalibrated regularly. Pump motors may need to be lubricated, according to manufacturer's instructions. Pump function may be assessed by noting the flowrate or sample volume, each time the unit is serviced. If either of these are seen to be falling over a period then it is possible that the diaphragm has torn or the carbon vanes are worn. A motor which has become noisy or is overheating probably has a bearing failed. Bubblers should be removed and thoroughly cleaned after each use. Sample lines which show reagent crystallized in them should be replaced, and brushes should be regularly checked, and replaced when necessary. In this case, "regularly" need not mean each time the unit is serviced, experience may show that the brush life is measured in months rather than days, so checks can be made every third or fourth service. It is vital, however that the frequency of checking should be such that deterioration in any part of a unit is detected well before a breakdown occurs, and the unit suffers damage.

The development of maintenance schedules and the repair of equipment is largely a matter of systematic thinking and organised common sense.

### 7.1.1 Logbooks

If a regular system of checking is to be undertaken, there is no real substitute for a maintenance logbook. Requiring an operator to note in a logbook that he has completed a task should never be regarded as a reflection on his personal integrity. It is not, it is merely an efficient manner of ensuring that an important check has been made. It ensures that if, say, an operator is absent on the normal day of servicing, then the servicing is not accidentally forgotten. This log may take the form of a simple notebook, in which details of maintenance and repair tasks are noted, as they are done, or, in the case of more complex instruments it may be a card, as illustrated in Figure 26. This covers a chemiluminescence instrument, used to monitor nitrogen oxides in the atmosphere. In this case, it might also be considered useful to have a logbook as well, to record dates on which any part is replaced in the instrument. This gives an indication of the life which may be expected from, say, a drive belt. Information of this type is needed in planning the number and types of spare parts which are to be held in store. The precise form the log takes is not important, the important thing is that it is kept, and kept up to date.

### 7.1.2 Maintenance of Adequate Spares

Consideration should be given to the number and type of spare parts which must be held in stock to maintain a programme efficiently. The first decision which must be made is whether a replacement for any particular part is likely to be needed, and if so the expected life of the part in question. For example, there is no need to have in stock a spare case for an instrument - instrument cases are not likely to break. Pump diaphragms have an expected life of over 12 months, so a limited stock only of these need be carried. A recorder chart...
...lasts about 1 month, so a larger stock of these is needed. Under dusty conditions, a line filter may last a few days at the most, so a larger stock again is needed.

Other considerations include the availability of the spare part, its cost, and whether bulk discounts are available. If a part is readily available from a store in the city, then there is no need to carry a large stock of these, enough to satisfy an immediate need is all that is required. If the part must be imported, or is on a long delivery time, then a large enough stock must be carried to ensure that the testing programme is not interrupted through instrument failure. For example, the rubber gasket of a high volume sampler requires periodical replacement. This is a specialized item, hence it is usually ordered from the instrument manufacturer, not from a local store. On the other hand, items such as fuses are so cheap that a larger stock can be carried. In many cases, bulk buying discounts are available, for example a carton of ten recorder charts is usually appreciably cheaper than ten charts, bought one at a time.

It is useful to establish in the laboratory store a table of maximum and minimum stocks. First decide the minimum number of an item which it is advisable to hold, say, for example, this is two. Suppose these items come in cartons of six. The maximum stock would then be eight. The storeman knows that when he sees two of these items left in stock, he is to order another six, to bring the stock up to its maximum.

7.1.3 Trouble Shooting

In spite of any maintenance schedule which is developed, instruments will fail from time to time, and repairs will be needed. But first, the cause of the failure must be established. Again, this is largely a matter of systematic thinking and common sense. More complex electronic monitoring equipment should always include in the operational manual a "trouble shooting chart", that is, an orderly list of steps which should be taken to find the component which has failed; a simple example of this is listed below. Suppose an operator visits the site where a sampling train has been set up to monitor sulphur dioxide. He finds no bubbles being drawn through the impinger, or that the reading of the gas meter is much lower than would be expected if the pump was functioning correctly. His investigation might follow the pattern below:

**Pump Trouble Shooting Chart**

1. **Disconnect pump from sample line, Turn on Power**

<table>
<thead>
<tr>
<th>Motor Runs</th>
<th>Motor does not run</th>
<th>Fuse Blows</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freely</td>
<td>Stiffly</td>
<td>Go to 2</td>
</tr>
<tr>
<td>Go to 7</td>
<td>Go to 6</td>
<td>Return motor to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrical Workshop for repair</td>
</tr>
</tbody>
</table>

2. **Check Power Point. Is there voltage?**

<table>
<thead>
<tr>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Go to 4</td>
<td>Go to 3</td>
</tr>
</tbody>
</table>

3. **Check Fuse Is in intact?**

<table>
<thead>
<tr>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Go to 4</td>
<td>Repair fuse and return to 1.</td>
</tr>
</tbody>
</table>

4. **Turn off Power and remove Power Plug. Can the motor be turned easily by hand?**

<table>
<thead>
<tr>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Go to 5</td>
<td>Go to 6</td>
</tr>
</tbody>
</table>

5. **Check continuity of motor windings. Remove motor to electrical workshop for repair.**
6. Check shaft bearings and armature alignment.
   If the motor is overheating, this is a symptom of faulty bearings or
   the armature binding in the case. Replace bearings or realign shaft.

7. Motor runs, air flows through the pump at pressure.
   Yes  No
   Go to 8   Go to 9

8. Check for leaks or blockages in the sample lines or apparatus
   Seal leaks or clear blockages. Establish why they occurred.

   Check for faulty or sticking valves. Check for torn diaphragm or
   worn carbon vanes in the pump chamber.

These plans are by no means exhaustive, there are obviously other things
which can go wrong with sampling systems. However, they do illustrate the type of
approach which can be used in investigating a problem like this.

There is an additional investigation which may need to be made after the
instrument has been repaired. The operator should try to establish the real cause
of the failure, whether it was due to normal wear or whether there is some
malfunction present in the system, so that the same part may be expected to suffer
premature failure again. This information may be found in the maintenance
logbook; recurring failure of a particular part of the instrument indicates
that this should either be redesigned or that a stronger, higher capacity part
should be used in its place.

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**Figure 26 - Oxides of Nitrogen Analyser Maintenance Chart**
AIR QUALITY MANAGEMENT AND SURVEILLANCE

8. Role of Monitoring in Assessments

Monitoring helps to demonstrate the need for control (by establishing pollution levels), then guides the development of control strategies (by showing the degree of control needed) and finally indicates how effective the controls are (by allowing comparisons with established standards and/or by comparisons of "before and after" values).

Although there is a clear case for the establishment of a monitoring programme, nevertheless once the appropriate number of stations have been set up care should be taken to avoid the situation of over-commitment to this part of the overall air quality strategy. Monitoring costs are high, yet every additional station allows for further input of data to further refine our knowledge of the subject area. The difficulty is in striking a balance and in judging when the optimum point of "sufficiency" has been reached. Once it has the incremental increase in benefits which accrue from additional increments in the monitoring costs become progressively less and less. Yet this judgement must of necessity be subjective.

Monitoring is carried out by a chemical laboratory or technical services group which has routine and regular activities both within the laboratory proper and in the field. It also has demands placed upon it for rapid response to unfamiliar situations, nonroutine investigations and analyses and modifications and development of techniques and equipment.

Surveillance of air quality has become an increasingly important function of an air pollution control agency in recent times. Moreover, monitoring is usually the only programme element for which technical services take primary, rather than support responsibility.

8.2 Reduction and Interpretation of Data

Data must be summarized in a convenient format and be available when required. Values should be expressed in uniform units and reduced systematically to meaningful averaging periods.

A very important part of the entire monitoring effort is the validation of data. Whatever quality control procedures are used and whatever the care exercised during the sampling and analysis phase, erroneous or questionable values can still be generated. For this reason, all data must be subjected to careful scrutiny prior to further treatment or publication to enable discarding of erroneous data.

Ideally, the data reduction system should be flexible and responsive to diverse needs. The system should be capable of producing data averaged over \( \frac{1}{2} \) to 1 hour and other short periods as well as 8 hours, 24 hours, monthly, seasonal and yearly. It should make available the maximum concentrations for each of these averaging times.

Facilities and staff should be adequate to prepare and publish routine summaries of all data, to compile area-wide statistics, and to analyse the significance of the data.

8.3 Administrative and Legal Aspects

Two different approaches to the administration of air pollution control have evolved in different parts of the world. The basic philosophies are usually referred to as "best practicable means" and "air quality management".19

8.3.1 Best Practicable means

Adherents of the "best practicable means" approach assert that air pollution should be kept to a minimum per se. This implies the use of the best available and the most economically feasible technology to control sources of
pollution without referring (necessarily) to ambient air quality guides* and standards.

Determination of what constitutes the best available control technology involves consideration of not only the technology within a given industry, but also the technology of other industries. However, the consideration of feasible cost involves, inter alia, the effects on the environment and on human health, on the stage of socio-economic development, on the political climate and on public opinion. Therefore at least indirectly, some consideration is given to air quality.

Because it is more difficult to install controls on existing installations than on new plants, the adoption of the best practicable means approach may, in practice, lead to different requirements for new and existing old plants.

Often emission standards are used to define the best practicable means for single sources. It is obviously simplest if these standards are uniform for the whole country, particularly if technical and economic conditions are approximately uniform throughout the country. It must be appreciated, however, that with this approach anomalies will occur, as the ambient air quality will vary with the number and density of sources and with local meteorological conditions.

The major disadvantage of this system is, therefore, that it does not necessarily guarantee satisfactory air quality. This disadvantage is more theoretical than real however; in practice a watch is still kept on ambient air quality.

This "best practicable means" approach makes little demand on laboratory resources and requires a minimum of staff. These staff, however, must be of a high calibre because they are virtually acting in the role of consultants in air pollution control to the industries involved. A great deal has been done in the way of curbing major industrial sources of pollution by using this philosophy, where the circumstances favour a co-operative approach with industry.

In countries with limited resources, an approach combining the best practicable means and yet setting air quality goals and emissions standards has much to commend it.

8.3.2 Air Quality Management

The "air quality management" approach relates control requirements to the desired air quality. This is a more involved approach and requires a knowledge of existing source emissions and air quality in the area. A dispersion model for the area can be developed, taking into account the relevant meteorological parameters and such additional factors as the extent of future industrialization and urbanization, and town planning, energy and transport policies, to calculate future air quality. The severity of a control programme will depend upon the difference between the existing or predicted future air quality and the desired air quality standards or goals. Emission standards can then be determined, based on the desired reduction in emissions.

It can be argued that air quality management is a more logical and more scientific approach and also that it allows for the combination of various factors and policies into alternate programmes to achieve and maintain the desired air quality, therefore permitting long-term planning to avoid air pollution.

* "guides" are defined as sets of levels and exposure times that are associated with specific effects of varying levels of air pollution on man, animals, vegetation and the environment in general.
However, there are a number of drawbacks to the practical application of this approach. Present data on effects are incomplete, and decisions fixing ambient air levels have often to be made in a rather arbitrary fashion. There is also a margin of error involved in the adequacy of predictions made in the planning stages, particularly those concerned with emission inventories and dispersion phenomena. There is, therefore, the need for continuous reappraisal of the predictions as additional information on the performance of the controls becomes available.

The air quality management approach is much more demanding in terms of total manpower, the size of the air monitoring network, instrumentation, laboratory resources and other support facilities.

8.3.3 Air Quality Standards

"Ambient air quality standards" are guides which have been adopted by a country and made compulsory.

In 1972, the W.H.O. Expert Committee on Air Quality Criteria* and Guides for Urban Air Pollutants** considered that, owing to the uncertainty of the dose-effect relationships, the use of a safety factor is prudent, even when standards are derived from air quality guides. The magnitude of the safety factor would depend upon many factors. These may be political, with the main emphasis on cost-benefit analysis, or they may be related to the significance and reliability of the data, including whether the experimental evidence was obtained from animals or human beings. This Committee also recommended that the development of national air pollution standards should include both the standards to be met in a few years and also long-term goals. It was pointed out, however, that the concept of a standard to protect the population from significant harm is a statistical one. Obviously, the adoption of such a standard would not confer protection on every individual.

The degree of health protection which is selected above the minimum acceptable level is a matter for political decision. The governments concerned must make decisions on what they can afford at any point in time, taking into account the priorities imposed by other health problems as well as social, cultural and economic factors (including the stage of development of a country). Air quality standards, therefore, reflect what a community can or will afford.

Emission standards exist on a regional or national basis in many countries (the United Kingdom, New Zealand, Federal Republic of Germany, Sweden, Japan, Belgium, France, Australia, etc.). In many countries these standards are set in the absence of ambient air standards although in the "classical" air quality management approach, emission standards are calculated on the basis of the required ambient air standards (and existing ambient air levels, emission inventories, simulation models, etc.). However, there is an implied relationship to ambient air quality in that the emission standards are set in order to protect or improve the existing air quality.

An advantage of emission standards is the removal of ambiguity. They are convenient for the control agency to administer and furnish to the industrialist because, if they are realistic, meeting them is usually not technically complicated. They can also assume equality of sacrifice; one plant of a specific type is called upon to exert the same measure of control as a competitor. Emission standards may be applied equally to all sources, with only special exceptions, regardless of local circumstances.

* "criteria" are defined as the tests which permit the determination of the nature and magnitude of the effects of air pollution on man and his environment.
Emission standards are based mostly on the concentration of a given pollutant in the exhaust gas stream, but anomalies may occur at times in the absence of regulations governing the mass emission pollutants, particularly at very high and very low gas-emission rates. Other problems with emission standards relate to the variability of resulting air quality and also to the fluctuations in emission rates which occur in a great many cases from a variety of causes, including normal changes in the process, accidental escapes, control equipment malfunction and careless operation. A specific source may operate without causing excessive pollution most of the time, but still produce intermittently severely undesirable effects. Ambient air quality determinations are therefore a necessary adjunct to emission measurements, and a control programme based on emission standards must involve at least a basic air monitoring scheme (as well as the measurement of stack emissions).

Another complication of emission standards is the tendency to regard them as standards for the design of new plants. For new plants there may be good reason to establish a second, more rigid set of standards (to stimulate constant improvement of control equipment) or to introduce other mechanisms such as approval of the actual equipment in order to bring about constant improvement. This latter method places some share of the responsibility for effective control of emissions on the approving organizations.

In some countries, the formulae used to calculate the height of chimneys have been standardized, on the basis of the mass emission of sulphur dioxide.

Other standards aimed specifically at air pollution control have been developed in various countries. Fuel standards have been developed on a national or regional basis in some countries (the USA, United Kingdom, France, Italy, Sweden, etc.). These relate either to the type of fuel which may be used (examples are natural gas and smokeless fuels), or to limitations on the concentration of certain constituents within a given fuel (examples are specifications limiting the allowable volatile content of coals and the sulphur content of fuel oils).

There are also a number of design standards involving the creation of buffer zones of various widths around specific industries (in the U.S.S.R., Czechoslovakia, Poland, Romania, Israel, etc.). Sets of instructions or procedures pertaining to the implementation of air pollution control programmes for specific (limited) periods of time are also in use (for example in Israel, the Rhine estuary in the Netherlands, New York City, Los Angeles County and the Federal Republic of Germany).

8.3.4 Implementation of Air Pollution Legislation

For effective control, specific air pollution legislation should be provided at as early a stage as possible. Without control legislation, air pollution will tend to increase, and delays will make a deteriorating situation more difficult and expensive to resolve. The development of basic legislation can also provide a structure for the recruitment and training of staff.

Legislation might be directed towards:

(1) the control of sources of pollution by specifying the types of industrial and other processes which should operate under supervision by control authorities, and the types of emission which should be kept to a minimum value;

At very high gas flowrates, a given pollutant at a concentration less than the allowable limit may nevertheless have a highly significant mass emission; at very low gas flowrates, a given pollutant may have an insignificant mass emission even though the statutory concentration limit is exceeded.
Unfortunately, air pollution considerations have in the past received scant
control equipment. These usually take the form of allowing for exemption of part
different categories, usually on the type of industry and its potential to
pollute or on an increasing scale with the size of production.

Specification of the type of industry is usually accomplished by requiring
the registration of polluting factories. Fees are often charged for licensing
different categories, usually on the type of industry and its potential to
pollute or on an increasing scale with the size of production.

The requirement of the approval of plans for the control of air pollution
from new industrial plant or for significant changes in existing plant is often
built into the legislation. This provides a powerful tool to control future
pollution sources, but does not guarantee per se that a plant will later be
operated in strict accordance with the design requirements.

Taxation incentives have also been applied to the installation of approved
control equipment. These usually take the form of allowing for exemption of part
or all of sales or import taxes on control equipment, or else in allowing for the
accelerated discount of equipment for depreciation purposes.

8.3.4.1 Enforcement of Regulations

Ensuring compliance with legally enacted laws, regulations and
ordinances is part of the administrative function. It is self-evident
that air pollution control legislation must have "teeth" in order to
ensure compliance.

The enforcement of penalties varies markedly
in different parts of the world. For example, the traditional approach
of the British Alkali Inspectorate has been towards seeking a
co-operative approach with industry and using court action as the last
resort. On the other hand, in countries such as the United States of
America, court action is taken much more frequently.

There are also conflicting theories as to the relative magnitude
of the penalties which should be involved. One school of thought suggests
that high penalties act as a deterrent even though the maximum penalty may
not be invoked often. (Opponents of this philosophy assert that the
threat of high penalties tends to make any litigation expensive and
protracted.) The second school of thought reasons that although the fines
should be above a token amount, their magnitude should be so judged that
litigation is often avoided.

The type of approach to be used in any given country will depend
upon the political climate and the policy of the government.

The enforcement of the control in situations where there is no
specific law or regulation, such as annoyance reactions to odours, is far
more difficult because a subjective evaluation is required, and it is
therefore sometimes difficult to prove that a problem exists. In such
cases, much can be achieved by making provision in the legislation for
the control body to issue an order that certain measures, for example
installation of a specific type of control equipment, be carried out if,
in the judgement of its officers, this action is necessary to abate the
problem.

8.4 Local and Regional Planning

Unfortunately, air pollution considerations have in the past received scant
consideration in planning on either regional or local government levels in many parts of
the world. Indiscriminate sitings of dwellings and polluting factories and badly
corrected or haphazard policies with respect to motor-vehicle exhaust emissions and
transportation systems have produced conditions under which the people of certain areas
are exposed to potentially harmful concentrations of pollutants or there is serious
interference with their well-being and "quality of life" which could have been avoided.
There is also the corollary that in such situations, it is often necessary to employ
stricter control measures than may otherwise have been necessary.

8.4.1 Location of Industrial Plant

It is recognized that there are many other factors which the industrialist
must take into account when selecting a site. He must consider the availability of
raw materials, geographic resources, fuels and power, labour supply, proximity
to related industries and to markets, transportation facilities, et cetera.
Restrictions on location of industries must therefore be reasonable; otherwise
they will not be able to function, and a slowing-up of industrialization could be
detrimental to the overall standard of living.

Factors related to environmental pollution have acquired considerable
importance in recent years. Factory management has been forced to take a broader
view in site selection by the realization (whether forced by law or by other
pressures) that such selection should not have a degrading effect on the
community.

From an air pollution viewpoint, site selection should take into
consideration the nature of air contaminants, the efficiency of available control
devices, pertinent meteorological and micro-meteorological factors such as wind
directional frequencies, velocities at the locations under consideration and the
dispersive ability of the air at each possible site, the quality of the environ­
ment at that site and the potential effects on the surrounding areas.

It is now recognized that physically separating people from polluting
industries is good practice. This applies especially to air pollution and noise,
and is usually accomplished by the provision of suitable buffer zones of either
parklands or of light non-polluting industries. The extent of the buffer zone
depends upon the type and magnitude of the industry concerned and its potential
to pollute.

8.5 Public Information and Education

To ensure maximum impact of control legislation, it is important that a programme
of education be initiated at all levels of the community. In this context, it is as
well to remember the need for achieving acceptance by the persons being regulated as
well as by those adversely affected by pollution. If properly presented, controls
will be accepted by most polluters in the spirit that this is an obligation to the
community which they share with others. It is important that industrial organizations
should feel that they and their competitors are treated in a fair and consistent fashion
and they are performing a community service which will directly benefit their own
families and friends.

Often it is difficult to change an attitude of apathy towards air pollution in the
older generation, but education through the news media and through schools and civic
groups can achieve much.

In many large urban areas, a major cause of air pollution is the multitude of
sources (from industry, homes and motor vehicles) which are closely connected with the
everyday life of the community. Because control of these sources will require changes
in habits, and also economic implications for many people, a well-designed public
education and information programme, though difficult to achieve, is imperative. The
difficulties in finding a complete solution to particularly intractable industrial
problems should be explained; an informed public will also realize that it is
economically feasible to decrease pollution only to an acceptable minimum and that
unduly restrictive regulations based on emotion and not on fact hamper industries and
therefore lower the overall standard of living.
Companies responsible for industrial plants whose emissions can affect nearby residents also need to engage in public information activities in order to help the public to understand the special problems which the companies face in controlling emissions and their efforts to solve them.

A basic objective of the community information programme should be to convey an understanding of the air pollution control organization and its aims, objectives and problems.
9. SOURCES OF AIR POLLUTION AND TRENDS

Air is a mixture of gases consisting of approximately 78 percent nitrogen, 21 percent oxygen and a little less than one percent of argon. These three elements, together with carbon dioxide, 0.03 percent, total 99.99 percent of dry air. Table 3 summarises the concentrations in parts per million of the major and several minor gaseous components of the earth's normal dry atmosphere at surface level.

Table 3
Concentrations of Gases Comprising Normal Dry Air

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>780 900</td>
</tr>
<tr>
<td>Oxygen</td>
<td>209 400</td>
</tr>
<tr>
<td>Argon</td>
<td>9 300</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>315</td>
</tr>
<tr>
<td>Neon</td>
<td>18</td>
</tr>
<tr>
<td>Helium</td>
<td>5.2</td>
</tr>
<tr>
<td>Methane</td>
<td>1.0 - 1.2</td>
</tr>
<tr>
<td>Krypton</td>
<td>1</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.1</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.08</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>0.02</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.01 - 0.04</td>
</tr>
</tbody>
</table>

Water vapour is always associated with these gases; the moisture content of the air is variable and usually constitutes about 1-3 percent by volume of the total.

However, air sampled close to ground level often contains other gases, vapours and particulate matter (including aerosols). These arise both from man's activities and from natural causes.

Air pollution is generally considered to occur when, as a result of man's activities, enough of a substance is present in the ambient air to cause harmful effects to man or to the environment generally.

The principal man-made sources of atmospheric pollutants may be grouped as:

Combustion of Fuels:

.1 Stationary sources
.2 Motor vehicles and other mobile sources

Industrial Processes.

9.1 Combustion of Fuels

Although much fuel has been in the past and is still used wastefully, as shown for example by heavy emissions of smoke, economic pressures have resulted in improvements in the efficiency of most fuel burning equipment.

Fundamental Aspects of Combustion: In order to ensure complete combustion and absence of visible smoke from combustion processes, the following basic requirements need to be met:

(i) Correct proportioning of air and fuel; a certain amount of excess air over that theoretically required is necessary, and this amount progressively increases with
a change in physical state of the fuel from gaseous to liquid to solid. (O/F)

(ii) Temperature, which should be high enough to ensure early ignition and a
practicable rate of combustion.

(iii) Time, which should be sufficient to allow reactions to be completed.

(iv) Turbulence to ensure adequate mixing so that combustion could be completed with
the minimum amount of excess air and without stratification of combustible gases
and air.

(These are sometimes referred to as the "Three T's end OfF)

If one or more of the above requirements are not adequately provided, combustion
is incomplete and visible smoke is produced. More importantly, associated with the
smoke are also produced and emitted a range of invisible pollutants such as carbon
monoxide, methane and various hydrocarbons, many of which may be partially oxidized.
These pollutants are also a major and significant contribution to combustion losses,
thus reducing the efficiency of the process and resulting in important energy losses.

It is stressed that in many cases smoke production can be readily eliminated by
correcting the combustion process to satisfy the four basic requirements listed above.
For example, if the time allowed for combustion is insufficient because the furnace
chamber is too small or is being overloaded, combustion could be effectively completed
by raising the temperature and increasing the turbulence.

Formation of Nitrogen Oxides in Combustion Processes: The term NOx is often used
to cover the total amount of nitrogen oxides, particularly NO and NO2 found in the
atmosphere or in gaseous products of combustion. However, in combustion processes, the
predominant oxide formed (over 90% of the total) is NO.

The amount of NO formed is a function of:

(i) the nitrogen associated with the fuel;
(ii) the amount of excess air supplied; and
(iii) the temperature of the combustion process.

Little can be done to reduce the formation of NO from fuel nitrogen. However,
NO formation during the combustion process resulting from the nitrogen present in the
air may be reduced by modifying the combustion process in order to reduce the
temperature, the amount of excess air or both.

The NO produced from the combustion process is subsequently oxidized in the
atmosphere to NO2 with the NOx playing an important role in photochemical smog
formation and the production of secondary pollutants such as oxidants.

9.1.1 Stationary Sources

Fly ash is a problem when solid fuel is used; it consists mainly of
silica and alumina with small amounts of oxides of iron, calcium and magnesium
but may contain up to 30 percent of unburnt carbon. Particulate pollution is less
of a problem when liquid or gaseous fuels are used because of the more efficient
combustion and the much smaller amount of non-combustible material present in the
fuel. Nevertheless, heavy emissions of smoke can still occur with bad combustion
technology.

Apart from large amounts of normal atmospheric gases - carbon dioxide,
nitrogen, oxygen and water vapour - which are released from combustion processes,
the most common of the pollutant gases emitted are sulphur dioxide, sulphur
trioxide, carbon monoxide, nitric oxide, nitrogen dioxide, unconsumed hydrocarbons
and various partially oxidized hydrocarbon products.

Although most of the sulphur present in the fuels appears in the resulting
exhaust gases as sulphur dioxide (the SO3:SO2 ratio varies from about 0.016 to
0.074), the presence of sulphur trioxide is important because it significantly raises the dew point of the flue gases from about 60°C with no SO₃ to 182°C with 5 percent SO₃ and readily forms acid mist with the moisture in the atmosphere.

Typical emission factors for the combustion of bituminous coal, oil and natural gas are given in Table 4.

In many countries, domestic consumption of fuel for cooking and heating purposes can make a highly significant contribution to air pollution.

The burning of refuse can also add considerably to this form of pollution, especially from fires on open tips.

9.1.2 Motor Vehicles and Other Mobile Sources

Because of their large numbers, the petrol powered motor vehicle is the dominant source of air pollution in this category.

The concentrations of the main pollutants, carbon monoxide, hydrocarbons and oxides of nitrogen, vary widely depending upon the different operating modes. Some typical values are:

<table>
<thead>
<tr>
<th>Operating Mode</th>
<th>(Concentrations, in ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>Idling</td>
<td>64 000</td>
</tr>
<tr>
<td>Cruising</td>
<td>24 000</td>
</tr>
<tr>
<td>Acceleration</td>
<td>24 000</td>
</tr>
<tr>
<td>Deceleration</td>
<td>45 000</td>
</tr>
</tbody>
</table>

As the volume of exhaust gas also varies depending on the mode of operation, the weight of pollutant emitted per unit of distance travelled or per unit of time is a more satisfactory index. On the basis of grammes emitted per kilometre travelled, the range of typical emission factors for uncontrolled motor vehicles is:

- Carbon monoxide: 50-75 g/km
- Hydrocarbons: 5-8 g/km
- Nitrogen oxides: 2-4 g/km
- Particulate matter: 0.16-0.20 g/km

In older model cars, apart from emissions from the exhaust pipe and evaporation losses from the fuel tank and carburettor, up to 25 percent of the total hydrocarbons were emitted from the crankcase vent tube. Most modern vehicles prevent pollution from this source by recycling the vent gases. Increasing attention is also being directed towards minimizing evaporation losses from the fuel tank and the carburettor.

Lead emissions by motor vehicles are attributable to the tetramethyl and tetaethyl lead added to gasoline to prevent pre-ignition (knocking). The amount of lead in one litre of gasoline usually varies from about 0.5 - 1 gramme. Their decomposition products are discharged mainly as particulate matter. Regulations* for example, the concentration of hydrocarbons in the exhaust gas is relatively low during acceleration, but the weight of hydrocarbons emitted during this mode is greatest at that time because of the relatively larger volume of exhaust gas. Also, although the concentrations of carbon monoxide are least during acceleration and cruise conditions, because of the larger exhaust volumes, weight emissions of CO are greatest during these modes.
Table 4

EMISSION FACTORS FOR THE COMBUSTION OF BITUMINOUS COAL, OIL AND NATURAL GAS

(in kg/tonne of fuel consumed)

<table>
<thead>
<tr>
<th>Fuel and Type of Plant</th>
<th>Particulate Matter</th>
<th>Oxides of Sulphur (as SO₂)</th>
<th>Carbon Monoxide</th>
<th>Hydrocarbons (as C₄)</th>
<th>Oxides of Nitrogen (as NO₂)</th>
<th>Aldehydes (as HCHO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous Coal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power Plant and large industrial boilers (pulverised coal)</td>
<td>8A</td>
<td>19s</td>
<td>0.5</td>
<td>0.15</td>
<td>9</td>
<td>0.0025</td>
</tr>
<tr>
<td>General Industrial Boilers (spreader stoker)</td>
<td>6.5A</td>
<td>19s</td>
<td>1</td>
<td>0.5</td>
<td>7.5</td>
<td>0.0025</td>
</tr>
<tr>
<td>Commercial and domestic furnaces</td>
<td>1A</td>
<td>19s</td>
<td>5</td>
<td>1.5</td>
<td>3</td>
<td>0.0025</td>
</tr>
<tr>
<td>Handfired units</td>
<td>10</td>
<td>19s</td>
<td>45</td>
<td>10</td>
<td>1.5</td>
<td>0.0025</td>
</tr>
<tr>
<td>Oil Power Plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial and Commercial Boilers</td>
<td>0.94</td>
<td>18s</td>
<td>0.005</td>
<td>0.24</td>
<td>11.8</td>
<td>0.11</td>
</tr>
<tr>
<td>1. Residual Oil</td>
<td>2.6</td>
<td>18s</td>
<td>0.0025</td>
<td>0.33</td>
<td>4.5-9</td>
<td>0.11</td>
</tr>
<tr>
<td>2. Distillate</td>
<td>1.7</td>
<td>16s</td>
<td>0.0025</td>
<td>0.33</td>
<td>4.5-9</td>
<td>0.24</td>
</tr>
<tr>
<td>Domestic Units</td>
<td>1.1</td>
<td>16s</td>
<td>0.006</td>
<td>0.33</td>
<td>1.4</td>
<td>0.24</td>
</tr>
<tr>
<td>Natural Gas Power Plant</td>
<td>0.28</td>
<td>0.011</td>
<td>0.008</td>
<td>0.8</td>
<td>7.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Industrial Boilers</td>
<td>0.34</td>
<td>0.011</td>
<td>0.008</td>
<td>0.8</td>
<td>2.3-4.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Commercial &amp; Domestic Units</td>
<td>0.35</td>
<td>0.011</td>
<td>0.40</td>
<td>0.16</td>
<td>1.0-1.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

A equals the percentage ash in the coal. For example, if a power plant burns a coal of 10 percent ash, the emission factor is 80 kg/tonne.

s equals the percentage sulphur in the fuel. For example, if a power plant burns an oil of 2%, the emission factor is 36 kg/tonne.
limiting the amount of lead in petrol have been introduced recently in a number
of developed countries. The use of a lead filter or trap to physically remove
lead as particulate matter from the exhaust gases is another alternative being
considered.

Diesel Vehicles

Because they operate on an excess of air, diesel driven vehicles in theory
should produce little carbon monoxide or smoke and the gas emissions or smoke
which at times occur are nearly always caused by the mechanical condition of the
engine and ancillary equipment, together with the load and method of operation.
The most important source of diesel engine emissions is the exhaust, although
small quantities of hydrocarbons (10-15 ppm) escape from the crankcase in four-
cycle engines. According to various analytical studies, the composition of diesel
gine exhaust is approximately:

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>&lt; 1 000 ppm</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>100-600 ppm</td>
</tr>
<tr>
<td>Oxides of Nitrogen (as NO₂)</td>
<td>10-1 000 ppm</td>
</tr>
<tr>
<td>Aldehydes (as HCHO)</td>
<td>5-20 ppm</td>
</tr>
</tbody>
</table>

For heavy duty trucks, the emissions per kilometre are approximately:

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration (g/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>15-18</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>2.5-3</td>
</tr>
<tr>
<td>Oxides of Nitrogen (as NO₂)</td>
<td>13</td>
</tr>
<tr>
<td>Aldehydes (as HCHO)</td>
<td>0.2</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>0.7-1.0</td>
</tr>
<tr>
<td>Oxides of sulphur (as SO₂)</td>
<td>1.5-1.8</td>
</tr>
</tbody>
</table>

Emissions from Aircraft

Exhaust emissions from jet and piston aircraft include the same pollutants
emitted by motor vehicles and consequently participate in the same air pollution
problems.

The present contribution of aircraft emissions to the total atmospheric
pollution burden in the lowest 3000 ft. is considered to be small. Based on
emission densities the average level of atmospheric pollution at selected air
terminals and in their immediate vicinity is of comparable magnitude to that in
the communities in which the terminals are located. On the basis of studies
carried out in a number of places in the world, it is unlikely that the
contributions from aircraft in a given urban community will be more than about
1-2 percent of the total carbon monoxide or hydrocarbons or oxides of nitrogen
emitted into the atmosphere from other sources. The emission of aerosols may be
slightly higher.

Railway Locomotives

This source of pollution depends very much on the fuel used to operate the
locomotive. In many developed countries, steam locomotives have been replaced by
electric or diesel powered engines with a concomitant reduction in smoke
emissions. In other parts of the world where coal or timber fuel locomotives
are still in operation, a considerable amount of pollution as smoke and
particulate matter occurs near to the railway lines.
Shipping

The extent of pollution from shipping, like railway locomotives varies considerably from place to place. In many ports, smoke pollution is minimized by regulations governing the density of smoke which ships can emit while in harbour. Prevention of soot blowing in ports can also limit the degree of emission of particulate matter.

9.2 Industrial Processes

Emissions from industrial plant vary markedly with the nature of the industry and the type and magnitude of the plant. The following classes of works however are generally responsible for most of the emissions of significant quantities of particulate matter or gaseous pollutants:

Cement Works

Particulate matter is the main pollutant and is emitted from kilns, dryers, crushing operations, storage silos, transfer operations and boilers.

Brick and Ceramic Works

Emissions of particulate matter occur during the materials handling stages from the drying, grinding, transfer and storage operations. In the curing and firing operations, most particulate emissions occur from cool-fired kilns. The quantity of nitrogen oxides depends upon the method of firing but hydrogen fluoride emissions from fluorides present in the clay occur irrespective of the method of firing. Emissions of sulphur oxides are dependent upon the sulphur content of the fuel.

Grinding and Milling Works

Emissions of particulate matter occur from transferring, loading, storage and drying operations involving raw feed and ground product and in the grinding and milling operations themselves.

Chemical Works

Due to the diversity in the materials produced and consequently in the nature of the works, it is difficult to generalize. Potential emissions from many of these processes are high, but due to the nature of the compounds they are usually recovered as an economic necessity, or because of ambient air or emissions standards. Some of the more common gaseous emissions from this class of works include NOx, CO, H2S, RSH, Cl2, SO2, SO3, HF, HCl and hydrocarbons.

Metallurgical Works

The metallurgical industry is usually divided into the classifications of primary (production of metal from the ore) and secondary (production of alloys from ingot and scrap) metal production operations.

In primary operations, emissions vary markedly with the type of operation but in the case of iron and steel production, large quantities of particulate matter and carbon monoxide are produced. Large quantities of sulphur oxides (from sulphur in the ore) and particulate matter are usually emitted from smelting operations involving copper, lead and zinc ores. Fluorides (from the cryolite flux used in the reduction cells) and particulate matter are emitted from the aluminium reduction process.

Emissions from secondary metallurgical works involve particulate matter (coke particles, fine carbonaceous matter and metal fumes), together with products of combustion from the furnace heating operations and sometimes gaseous emissions from the flux. (e.g. Chlorine and chlorides from secondary aluminium smelting)
The most important factors affecting refinery emissions are the type of crude, refining capacity, processing scheme, and the nature and extent of air pollution control equipment. The major pollutants emitted are sulphur dioxide, nitrogen oxides and particulate matter from boilers and process heaters, carbon monoxide from catalytic cracking units and hydrocarbons from processing and transfer operations, storage vessels, pumps, glands and similar sources.

9.3 Trends in Air Pollution

9.3.1 Developed Countries

Twenty-five or thirty years ago, in many of the developed countries in the world emissions from the combustion of fossil fuels and from industrial processes were, relatively, more significant and constituted the more serious aspects of air pollution. The harmful effects of smoke, soot and grit emissions and sulphur oxides, were felt particularly in cities in Europe. Since that time, two factors, especially, enabled reductions to be made in particulate matter and smoke density.

A substantial increase in public awareness and consequent actions has probably been the most important single cause and this has been aided by the fact that real improvements in control were not technologically difficult to achieve nor unduly expensive. The other major cause was the increased usage of oil-based fuels and to a lesser degree natural gas at the expense of the traditional bituminous and sub-bituminous coal sources.

Reduction of sulphur dioxide emissions is much more difficult to achieve than control of particulate matter or smoke and as a further complication the fuel oils which replaced some of the coal were often as high or higher in sulphur content even after allowing for the increased calorific value of the oil-based fuels. The net results of this has been that except where natural gas or low sulphur fuel oils are dominant sources of energy, concentrations of sulphur dioxide have not materially improved; indeed, in a number of areas they have worsened.

Prior to the early 1940's, when the manifestations of photochemical smog first became evident in Los Angeles, little attention was paid to the motor vehicle as a source of atmospheric contaminants. In the years immediately following, photochemical pollution was still looked upon as a phenomenon peculiar to this location.

However, during the past decade photochemical pollution has become evident in many more cities in the world and the concern about this form of pollution has increased to a corresponding degree. To a large extent, the incidence of photochemical pollution can be related to large increases in the numbers of motor vehicles (in turn this is related to increases in population particularly in urban areas) and to increases in engine size. The development of improved monitoring systems for ozone and for oxidants has also had a substantial impact.

The relative importance of pollution arising from motor vehicles as opposed to combustion processes in stationary sources and industrial processes generally varies very much from place to place although it would probably be true to say that the motor vehicles have become the principal source of carbon monoxide, oxides of nitrogen, lead, hydrocarbons and oxidants in many of the larger urban communities. Measures are being taken in several countries to limit emissions of these pollutants by the imposition of increasingly stringent vehicle emission standards. While in some cases these have been moderately successful, mostly they have simply held pollution at the present levels (being balanced by increased numbers of motor vehicles) rather than result in any dramatic decrease in the concentration of pollutants.

Again the recent rise in petrol cost has resulted in a trend towards more efficient, smaller car engines and this factor in the short term will again tend
9.3.2 Developing Countries

In developing countries, fuel combustion, from industrial, commercial and domestic sources and from refuse disposal, is often the principal source of atmospheric pollution. Domestic cooking and heating in particular can often make a highly significant impact on levels of smoke and suspended particulate matter. As industrialization proceeds, increasing contributions can be made by fertilizer industries, power plants, metallurgical works and chemical and petrochemical complexes.

Although thirty years ago pollution from motor vehicles was usually of lesser importance, due to the relatively small number of motor vehicles, this is no longer the case. In fact, in many of the larger urban areas pollution from motor vehicles has now become a major problem. Vehicle numbers have grown substantially and although the number of vehicles per head of population is still somewhat smaller than in most developed countries, this is compensated by other factors.

Many vehicles are old, poorly maintained and have a low power to weight ratio. In many cities, motor bikes, motor scooters and derivatives of these make up a substantial proportion of the total vehicle population.
10.  EFFECTS OF AIR POLLUTION

10.1  Effects on Health

In assessing the possible health effects of air pollutants due care must be taken to compensate for such other components as smoking and occupational exposure, climatic, entropometric, socio-economic, nutritional and general environmental factors.

The acute episodes of pollution involving loss of life and serious injury have fortunately been rare but the health implications are that in the absence of control measures these episodes would be more likely to occur in the future. Whereas exposure to unusual accumulations of concentrations of irritant pollutants can cause measurable health effects long continued exposures to lower concentrations of the same or similar materials are more difficult to evaluate. Our detection levels may not be sensitive enough to show the effects of "normal" concentrations of pollutants.

Individual differences in response to air pollution are observed in all populations and generally speaking susceptibility is greatest among the newborn, the elderly and the infirm. Of the latter, a particularly sensitive group are those with pre-existing lung or heart disease. Because of the wide variation in sensitivity of different groups in the population, therefore, data concerning the health effects on healthy persons may not be as important as data on the groups of people most likely to be sensitive.

It should also be borne in mind that because of the increase in urban pollution in recent decades as yet insufficient is known about the effects of exposing people since birth to heavy concentrations of urban air pollution.

10.1.1  Mechanisms of Pollutant Action and Absorption by the Respiratory Tract

The respiratory tract, within which inhaled foreign material may come into intimate contact with the body's circulating blood, has a number of defences.

Larger and heavier particles are deposited by impaction and settlement in the nasal cavity and upper respiratory tract. Generally, particles of this size are similar to those that are deposited in dust-fall jars used for environmental sampling. Since these particles do not reach the deeper parts of the lung, their long-term effects are probably relatively unimportant, although they may have adverse effects on health through foreign-body reactions.

The smaller particles (less than about 3 μ) usually pass through the upper respiratory tract to reach the deeper parts of the lung. There they may be dissolved, if soluble or ingested by phagocytes if insoluble. They are sometimes deposited peripherally, or filtered out by the lymph nodes. If the particles are one of the forms of quartz, or some other minerals, they may ultimately lead to fibrosis or granulomatosis.

Thus it is particle size, or more precisely, the falling velocity of the particles that determines which part of the respiratory tract receives what dose and type of particulate pollution.

By contrast, solubility determines what portion of the respiratory tract becomes the main target for gaseous pollutants. In high concentrations, most of the inhaled sulphur dioxide for example is absorbed by the mucous membrane of the nose and upper respiratory tract, but as the concentration decreases, a small fraction of the inhaled dose is absorbed by the airway. An inhaled irritant gas that is highly soluble in water is likely to be dissolved in the aqueous fluids in the upper portion of the respiratory tract. However, such solution of the gas can be greatly modified by the presence of aerosols in the inhaled air. Thus, a gas which would normally not be carried beyond the trachea and large bronchi may be absorbed by or adsorbed on aerosols and thereby conveyed into the deeper parts of the lungs. Impingement of the aerosol or desorption may then occur allowing the gas to act upon the epithelial lining.
Particulate matter (even if chemically inert) and gases such as sulphur dioxide are capable of causing changes in airway calibre measureable by their effects on resistance to airflow. It has been shown in animals that inert particles of sodium chloride, which alone had little effect, could greatly augment the effect of sulphur dioxide on airway resistance. From this work have grown many additional studies of the effects of particle and gas combinations.

Three general principles predominate. First, the particle surface is thought to be a place where gas molecules can react. An example is the oxidation of sulphur dioxide to sulphur trioxide, which is catalysed by the action of manganese or ferric ions in the dust. The second mechanism is the concentration of gas and liquids on a particulate surface. Thus, the local concentration of pollutant molecules where a particle impinges on the surface of an airway or alveolus may be much higher than the average predicted from the assumption that the pollutant molecules would be uniformly distributed throughout the inhaled air. The third mechanism is the ability of particles to carry pollutant molecules where they might not otherwise be carried. For example, it has been shown that 3, 4 benzopyrene is bound so firmly to fine soot particles that the substance may be carried deep into the lungs and retained there for many days.

The lungs may react in various ways. Extreme airway-calibre changes occur in asthmatics. Secretion of mucous is one mechanism for buffering and dissolving gaseous pollutants and trapping particulate pollutants. Chronic bronchitis is a persisting and exaggerated form of this defense mechanism. The effect on the mucous membrane can lead to its secretory layer being thickened or its secretion being thicker or more viscous. The ciliary beat may be directly affected. This has been demonstrated experimentally in animals after exposure to high concentrations of some substances in polluted air. If the layer of mucous is thick and the rate of transport slowed, inhaled substances may remain in the lungs after the initial deposition.

Further studies are needed on the effect of different air pollutants on the clearing capacity of the lungs, and on the effects on ciliary activity and on thickness and viscosity of the mucous.

10.1.2 Long-Term Dangers of Air Pollutants

There have been a number of reports of long-term respiratory tract-effects with a suspected relationship to air pollution. Epidemiological studies of cardio-pulmonary conditions and respiratory function must be supplemented with controlled human and laboratory exposures at realistic levels and with realistic combinations. Such studies in each instance must take into account the role of cigarette smoking, of occupational exposures, and of extraneous variables before a "cause-effect" relationship of air pollution and chronic respiratory conditions can be accepted.

Bronchitis morbidity and mortality in Great Britain have been related to air pollution by a series of careful studies. In similar studies in other countries, chronic cough and sputum alone have been shown to have a similar prevalence in many areas with different levels of pollution and these symptoms occur more frequently in cigarette smokers than in non-smokers. However, the frequency of shortness of breath and protracted episodes of respiratory disability was greater in London than in rural England or cities in other parts of the world. Respiratory function tests give a similar pattern. Similarly convincing evidence has been presented from Japan that chronic respiratory conditions are more frequent in polluted areas.

In the United States of America, emphysema is a more frequently reported cause of death in urban than in rural areas. The relationship of emphysema to air pollution is not yet proven as clearly as for chronic bronchitis, but possible differences in the reporting of chronic bronchitis and of emphysema may account in part for this.
Other studies, on children, using nutritional and respiratory function
tests have shown that anaemia, morbidity, altered development and respiratory
conditions may be associated with air pollution.

There is also evidence suggesting a possible relationship between air
pollution and lung cancer, although scientific opinion is mostly that its role is
small in comparison with cigarette smoking and some occupational exposures.

10.2 Effects on Plants

Vegetation damage depends on many factors such as the plant species and stage of
growth, the nature of the pollutant, its concentration and time of exposure. The
position is complicated because of the other vectors operating, namely climate, soil,
insects, plant diseases and genetic history. The nature of the injury varies with the
toxicant but is usually some form of chlorotic marking or other colour change, leaf
tissue collapse with necrotic patterns and growth alterations.26

With sulphur dioxide, acute injury does not occur below 0.25-0.30 ppm over an
indefinite time period. Chronic injury may occur at concentrations between 0.1 and
0.3 ppm for varied time periods to sensitive plants. With ozone, sensitive varieties
respond to concentrations above 0.05 ppm for 1-2 hours. Peroxyacyl nitrates cause
damage at concentrations as low as 0.5 ppm. Ethylene at concentration of 0.1 ppm for
several hours damages tomato plants and retards growth at 0.05 ppm for several weeks.

Because fluorides act as an accumulative poison in the leaf tissue, time-
concentration factors need to be considered. Injury has been caused to gladiolus at an
exposure of 0.1 ppm for 5 weeks which corresponded to a leaf concentration of 150 ppm.
However forage may be rendered unsafe for animal feeding if more than 50 ppm fluorine
(on a dry basis) is absorbed. Nitrogen dioxide causes growth retardation at 0.5 ppm
and direct damage occurs at concentrations of 2-6 ppm for 2 hours.

Systems based on injury to sensitive plant species have been used as indicators of
the harmfulness of pollution to human well-being. The effects for example of sulphur
dioxide on alfalfa or lichens, of fluorides on gladioli or of ethylene on the flower of
the tomato plant are specific and semi-quantitative, although an experienced plant
pathologist may be required to differentiate the effects of pollution from those of
plant diseases, climatic changes or soil conditions. The effects of photochemical air
pollutants on annual blue grass (poa annua) and pinto bean (phaseolus vulgaris) have
been used to detect and estimate ozone and peroxyacetyl nitrate in mixtures. In
addition, biochemical studies on plants help in the study of the effects of pollutants
on human biochemistry.

10.3 Effects on Animals

Animals can be affected by the inhalation of pollutants in similar fashion to
human exposure. For example, a number of prize cattle were severely affected during the
1952 London air pollution episode. Some died or were subjected to emergency slaughter
and others developed symptoms which were attributed to air pollution. Post-mortem
examinations revealed acute bronchiolitis, emphysema and heart failure.27

However, the most significant route is usually the additional two-stage process
of accumulation of the airborne contaminants in vegetation and forage and the subsequent
ingestion by animals of the contaminated vegetation.

The pollutants responsible for most livestock damage are fluorides and to a lesser
extent arsenic. The major air pollution source of fluorides has been from industrial
plant, notably aluminium reduction plants (cryolite, Na3AlF6, flux is used in the
electrolytic cells) and superphosphate works. Arsenic poisoning of livestock near many
industrial processes and smelters has mostly been traced back to the ores or coal used
in combustion processes. Sheep have been poisoned by as little as 0.25-0.50 g of
arsenic daily. In laboratory experiments, 10 mg of arsenic per kilogram of body weight
per day has produced chronic arsenic poisoning in guinea pigs.

* The moral is not to graze your guinea pigs near a smelter
10.4 Effects on Climate

The principal determinant of weather and climate is the energy balance between incoming visible solar radiation absorbed by the earth's surface and atmosphere and the energy radiated back to space at longer wavelengths.26

10.4.1 Temperature Rise Due to CO2 - the "Greenhouse Effect"

Because CO2 in the atmosphere absorbs little incoming solar radiation, but is largely opaque to some long wavelength radiation emitted by the earth's surface, when CO2 concentrations increase, heat loss through radiation from the surface is reduced.

10.4.2 Temperature Fall Due to Particulate Matter

Increased concentrations of particulate matter and aerosols due to man-made activity act to decrease the radiation which reaches the earth and increase the frequency of fog and low cloud layers by acting as condensation nuclei.

10.4.3 Effects on Urban Atmospheric and Weather Conditions

From a considerable body of data collected over many years, it is evident that the climate of cities varies from that of adjacent rural areas. Moreover, there is increasing evidence that man-made activities may play an increasingly important role in this climate modification. Some of these effects are:

- Annual mean and winter maximum temperatures are both higher in cities than in the nearby countryside;
- The frequency of low level cloud and the incidence of fog are appreciably more;
- Rainfall is more and wind speeds, whether on an annual mean basis or as extreme gusts, are lower in cities (the latter is partially due to an increase in surface roughness in built-up areas).

Not all of these effects are attributable solely to air pollution. A significant factor in the "heat island effect" is the retention of solar heat in buildings and pavements. Apart from the particulate matter acting as additional condensation nuclei, the increased thermal energy in urban atmospheres causes air to be pushed up to colder levels, thereby aiding precipitation.

10.5 Other Effects

Direct damage to structural metals, surface coatings, fabrics and other materials is a widespread effect of air pollution. (In some instances, priceless historical buildings have suffered considerable surface damage and this aspect is causing considerable concern in some parts of the world.)

Although the principal agents are acid mists, or particulate matter containing acidic material, sulphides and oxidants also contribute. The latter for example cause extensive damage to rubber goods and textiles.

The soiling of a surface differs from property damage in that a soiled surface may be restored to its original form. However, the cost of removing dirt and soot is expensive, and in some areas prohibitive, thereby seriously affecting the whole amenity of the area.

Other effects include reduction in visibility and in aesthetic values which may at times have a profound effect on our expectations for an acceptable "quality of life".
11. TRANSPORT, DISPERSION, TRANSFORMATION AND DEGRADATION OF POLLUTANTS

The movement of contaminants by the atmosphere is governed by the wind speed and direction and the inter-related vertical and horizontal temperature gradients in the atmosphere, both of large and small scale. Essentially, the greater the wind speed the greater is the turbulence and the more rapid and complete the dispersion of contaminants in the atmosphere.

At most continental locations, the night hours are periods of low-level stability. As a result of the negative buoyancy and the increased energy required for vertical movements, pollutants disperse slowly and may be confined in relatively small volumes. The daytime winds are apt to be more gusty and of higher speed and the vertical movements are enhanced by solar heating of the earth which gives rise to thermal turbulence.

The local winds may differ markedly from the general air flow that characterizes the region. Along the coasts of continents or the larger lakes, the temperature differential between the land and water is sufficient to establish local circulations from the sea to the land during the day and from the land towards the sea during the night (however, the effect, particularly the sea-land convection wind, dies out generally within about 8-10 km from the coast). In the temperate latitudes these sea-breeze regimes are well marked only during the summer, and are masked by the general wind flow during the other seasons. However, in tropical and sub-tropical areas, they may be the dominant weather pattern.

The topography of an area may be extremely important, but as illustrated by the London acute episodes of pollution, the absence of restrictive topography does not preclude extreme pollution levels from occurring when the atmospheric stagnation exists for several days and when the source strength is sufficiently high. However, most major pollution episodes have occurred in areas where the air flow was markedly restricted by terrain, so that the flow was continuously channelled to a single direction or confined in a relatively small area. Within a fairly narrow valley, the characteristic daily wind pattern is (anabatic) flow up the slopes in the daytime, due to solar heating with (katabatic) flow in the reverse direction at night. Moreover, contaminants emitted near the floor of the valley under a temperature inversion may become effectively trapped within this area for long periods. The shielding from the effects of general circulation patterns afforded by the valley walls will result in lower wind speeds in the valley floor than would be the case in comparable level terrain.

11.1 Atmospheric Diffusion

Dilution of air contaminants in the atmosphere is of prime importance in the prevention of undesirable levels of pollution. In addition to dilution, other self-purification mechanisms are at work such as atmospheric scavenging, chemical and photochemical reactions, etc.

Turbulence, or eddy motion is the principal mechanism by which effective atmospheric diffusion is achieved. The rate of eddy diffusion is generally about three orders of magnitude greater than the rate of molecular diffusion and the latter effect is only significant under conditions of prolonged atmospheric stagnation.

Eddy motion consists essentially of two components - mechanical and thermal turbulence; mechanical turbulence is induced by movement of the wind over the surface of the earth and is proportional to the roughness of the surface and the wind speed. Thermal turbulence is solar-induced and is a function of latitude, the radiating surface and the stability of the atmosphere.

11.2 Lapse Rates

The rate of decrease in air temperature with altitude or "lapse rate" is of fundamental importance in air pollution considerations. The reference lapse rate which determines whether vertical mixing is enhanced or retarded is the "adiabatic lapse rate".
In well-mixed, dry air this rate is 0.98°C/100 m, referred to as the dry adiabatic lapse rate.*

The two most important conditions from an air pollution viewpoint are the superadiabatic lapse rate and the negative lapse rate or "inversion". In a clear day with strong solar heating of the earth, the lapse rate often becomes superadiabatic in the lower layers and the temperature decreases at a rate greater than the adiabatic rate. Under these conditions, vertical mixing and turbulence are at a maximum and the dispersion of pollutants is usually effective, although the rapid looping of exhaust plumes from chimney stacks can cause serious problems where it impinges on receptor areas.

The condition of temperature inversion wherein relatively warmer lighter air overlies cold air (hence an increase in air temperature with height) results in minimum turbulence and marked atmospheric stability. This occurs often on clear nights with light winds when the air next to the earth is cooled by nocturnal long-wave radiation. Inversions can also be formed aloft, for example, by the general subsidence (and subsequent compression and heating) of air over a fairly wide region.

Lapse rates usually follow a distinct diurnal pattern, namely low level radiation inversions occurring at night time and in the early hours of the morning are broken by thermal currents emanating from the ground by about 9 - 10 a.m. (During the so-called "fumigation" period, when the inversion is breaking up high concentrations of pollutants can occur at ground level for a short time.) These are replaced by near adiabatic lapse rates and later by superadiabatic lapse rates in the early afternoon when the surface heat is greatest.

However, when inversion conditions persist for a number of hours or even days pollutant concentrations tend to build up because of the absence of eddy diffusion. Particularly stable conditions occur when stagnating subsidence inversions overlay low level radiation inversions.

11.3 Transformation, Degradation and Atmospheric Scavenging

Substances emitted into the atmosphere are subjected to a variety of physical and chemical influences which affect both their conversion to other products and removal from the atmosphere by atmospheric scavenging processes.

The available routes for scavenging of foreign material from the atmosphere consist of deposition and conversion to normal atmospheric constituents. Chemical reactions facilitate both processes; the former by oxidation and combination of pollutants to give solid or liquid particles, or adsorbed phases on such particles; the latter through chemical and photochemical oxidation of more complex gaseous or vapour molecules.

* By definition, this is the lapse rate of a parcel of dry air as it moves upwards in a hydrostatically stable environment and expands slowly to lower pressure without exchanging heat with its surroundings. So long as the air is unsaturated, the approximation of the adiabatic lapse rate by the dry adiabatic lapse rate is satisfactory for most purposes. When the air is saturated, adiabatic cooling is partially offset by the release of latent heat. The relevant reference is then the saturation adiabatic rate which varies with temperature and height, but is approximately 0.56°C/100 m. 9

In this context it is important to distinguish between primary and secondary pollutants. Whereas primary pollutants are those emitted directly to the atmosphere, secondary pollutants are formed by chemical or photochemical reactions of the primary pollutants after the latter have been emitted into the atmosphere. Hydrocarbons and nitric oxide are examples of primary pollutants while peroxyacetyl nitrate and ozone are examples of secondary pollutants. Other pollutants such as nitrogen dioxide and aldehydes fall into both categories.
11.3.1 Particulate Matter (including Aerosols)

Four mechanisms appear to be responsible for removal of particles from air in the troposphere, namely:

(i) gravitational settling which not only prevents large particles, > 20 μm, from being transported very far but it also brings smaller particles to the vicinity of the surface;

(ii) impaction near ground level on the surface of obstacles such as trees and buildings;

(iii) coagulation or interception during the formation of cloud condensation nuclei;

(iv) interception by raindrops of particles larger than about 2 μm.

Hygroscopic substances such as sodium chloride and sulphuric acid mist grow substantially in size under conditions of high relative humidity, and may therefore be brought to the ground by rain much more effectively than by gravitational settling. Also, hygroscopic gases and mists are often present adsorbed on the surface of solid particles and can contribute in similar fashion to the removal of these particles.

11.3.2 Gaseous Constituents

11.3.2.1 Sulphur Oxides

From a study of the sulphur cycle it has been estimated that the average residence time of sulphur dioxide is about six weeks. Fossil fuels contain sulphur ranging from very small percentages to upwards of 4 - 5 percent in some heavy oils. When these fuels are burned, sulphur dioxide accounts for nearly all of the subsequent emissions of sulphur oxides (SO₃ : SO₂ ratios vary usually from about 0.016 to 0.074). At the relatively high concentrations in exhaust stacks, fairly rapid oxidation to sulphur trioxide occurs, probably catalysed by metallic constituents in fine ash particles. However, turbulent diffusion lowers the SO₂ concentration quite rapidly to only a few parts per million at only a few hundred feet from the source.

In experimental studies of the rate of oxidation of SO₂ in fog droplets, it has been estimated that in the presence of suitable catalysts such as ferric or manganous ions, rates of oxidation could be sufficient to account for the sulphuric acid content of some urban fogs. Photo-oxidation of sulphur dioxide at the concentrations normally found in ambient air is also slow, estimates in intense natural sunlight ranging from about 0.1% per hour to 0.4% per minute but this rate increases sharply in atmosphere containing automobile exhaust and olefines in the presence of oxides of nitrogen.

It would appear that the predominant mechanism, i.e. catalytic or photochemical and the degree of oxidation are determined by a number of factors including the concentration, residence time in the atmosphere, temperature, humidity, the intensity and spectral distribution of incident radiation and the presence of other pollutants such as metal oxides or ions, hydrocarbons and oxides of nitrogen.

Once some oxidation has occurred, the sulphur trioxide reacts rapidly with water vapour to form sulphuric acid mist:

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$$

This either absorbs water vapour and grows to a size where removal by gravitational settling or by interception with rain drops is
facilitated or reacts with other atmospheric constituents to yield sulphates (particularly ammonium and calcium sulphates) which are removed as particulate matter.

11.3.2.2 Oxides of Nitrogen

Nitrous oxide is present as a normal atmospheric constituent in concentrations of approximately 0.5 ppm but its inherent stability makes it unlikely that it plays an important role in low level atmospheric reactions. Of the other two oxides normally present in the air, NO and NO₂, by far the greatest amount is formed by high temperature combustion processes which result mostly in NO. At equilibrium conditions, most of the NO is oxidized to NO₂ but at the low concentrations occurring in the atmosphere the oxidation rate is slow. For example, 50 percent conversion to NO₂ takes 1000 hours at 0.1 ppm NO. However, photochemically nitrogen dioxide is strongly active and absorbs light over the visible and ultra-violet range of the solar spectrum, dissociating into nitric oxide and atomic oxygen:

\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \]

In the lower atmosphere oxygen atoms formed in this manner react with molecules of oxygen to form ozone:

\[ \text{O} + \text{O}_2 + \text{m} \rightarrow \text{O}_3 + \text{m} \]

(m is an energy accepting body)

Subsequent reactions in the system are complex, but the following overall equilibrium has been established:

\[ \text{NO}_2 + \text{O}_2 \rightleftharpoons \text{NO} + \text{O}_3 \]

When a reactive hydrocarbon such as an olefine or an alkyl benzene, both of which are emitted in automobile exhaust, is added to the system, a highly complex set of reactions ensues. These reactions lead to the production of a host of compounds characteristically found in photochemical smog. As well as ozone, these products include aldehydes, peroxyacyl nitrates and nitrites* and various nitrated olefines.

Nitrogen dioxide is thought to be converted to nitric acid either by subsequent oxidation to N₂O₅ and hydration or by hydration and catalytic oxidation in fog droplets:

\[ 2\text{NO}_2 \rightarrow (\text{O}) \rightarrow \text{N}_2\text{O}_5 \rightarrow \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]

The nitric acid then reacts with alkalies in the atmosphere to yield nitrate aerosols.

* R(CO)OONO₂ and R(CO)OONO respectively
11.3.2.3 Carbon Dioxide and Carbon Monoxide

Biological processes provide a natural system for the disposal as well as the partial replenishment of carbon dioxide. Another major influence on carbon dioxide removal is thought to be by solution in the oceans which are estimated to contain 60 times as much carbon dioxide as the atmosphere.36

Background carbon monoxide concentrations in the lower atmosphere range from about 0.01 to 0.2 mg/m³ with mean values around 0.1 mg/m³.37 These background levels have been obtained at several widely separated geographical locations. Despite the large generation of CO from natural and man-made sources which would otherwise account for an increase of 0.3 - 0.4 mg/m³ per year CO levels have not increased. A number of possible "sinks" or removal processes have been suggested to date, but for the most part these are highly speculative. They include oxidation to CO₂ by short-wave radiation in the upper atmosphere; metabolism by terrestrial and marine plants and micro-organisms; the binding of CO to porphyrin compounds in plants and animals with subsequent oxidation to CO₂; interaction between CO and ocean water or some agent in ocean water; and the adsorption and subsequent oxidation of CO on various surfaces.

11.3.2.4 Other Gases

Organic molecules photochemically produced in urban atmospheres as well as organic primary pollutants which may be emitted into the general atmosphere are subject to the atmospheric oxidation processes which eventually degrade most of these substances to carbon dioxide and water. However, because of the long time required to fully oxidize most of these compounds (and because the end products are natural constituents of the atmosphere), intermediate reaction products are of more concern. Some of these may accumulate to appreciable concentrations if their consuming-reactions are not sufficiently rapid, aldehydes are an example. The more reactive compounds are efficiently scavenged even though their rates of formation may be high. Compounds which are relatively slowly oxidized may be incorporated into the suspended particulate matter by polymerization and adsorption reactions and subsequently removed by scavenging of these particles.

Other gases which readily participate in chemical reactions are removed fairly rapidly (examples are hydrogen sulphide and ammonia which form sulphides and ammonia salts respectively).
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