Chapter 4

Air Pollution Measurements, Emission Estimates

One facility, two very different emissions

Sampling, Analysis, Monitoring as part of Air Quality Management:

WHAT ARE EMISSIONS?

- The amount of pollutant(s) a source puts into the air during a fixed time.
  - Units: mass/time
- Emissions vary; making air quality management a challenge!

Emissions vary over:

- **Time**
- **Location**
- **Pollutant**

These influence source emissions:

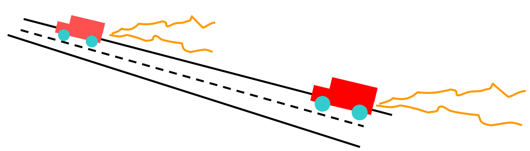
- **Source activity**
- **Economic health**
- **Population**
- **Climate**
- **Controls**
- **Traffic**

Classification by Source Type

1. Stationary sources
2. Mobile sources

Mobile

Mobile source



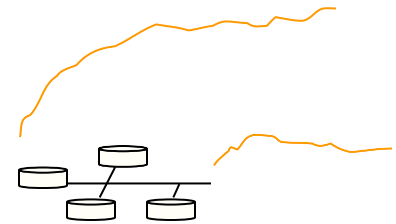
Examples: on-road: gas, diesel; off-road: marine, air, agricultural

Stationary

Point source

Examples: power plant, chemical plant, etc.

Area source



Examples: gas stations, dry cleaners, fireplaces, lawn mowers, tanks farms, etc.

Air Pollution Sampling/Measurement

- Source testing vs. ambient air monitoring
  - Both needed for:
    - Air quality standards
    - Pollution control devices performance
- Reporting concentrations & emission rates
- Types of samples
  1. Grab sample
  2. Continuous sample (1, 8, 14 hr, annual averages
- Isokinetic sampling (PM_{10}, $PM_{2.5}$)
- Representative samples may be more difficult to get than sample analysis

AIR POLLUTANT SAMPLING

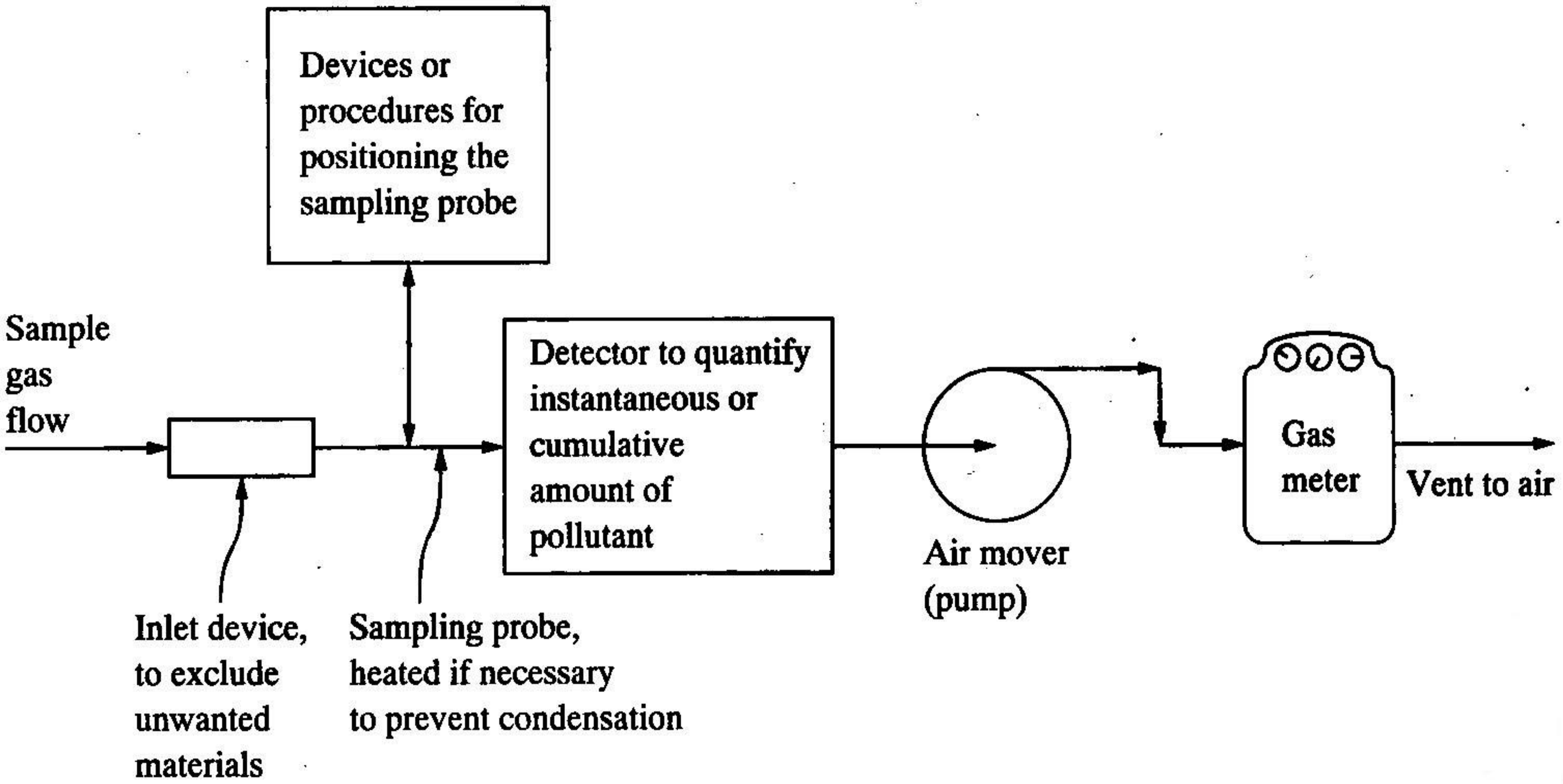


FIGURE 4.1
The components of any ambient-monitoring or source-sampling device. If the detector functions in real time (not cumulative), then the gas meter is not needed, but some kind of signal integrator or recorder is.

Location of air samplers, monitoring stations

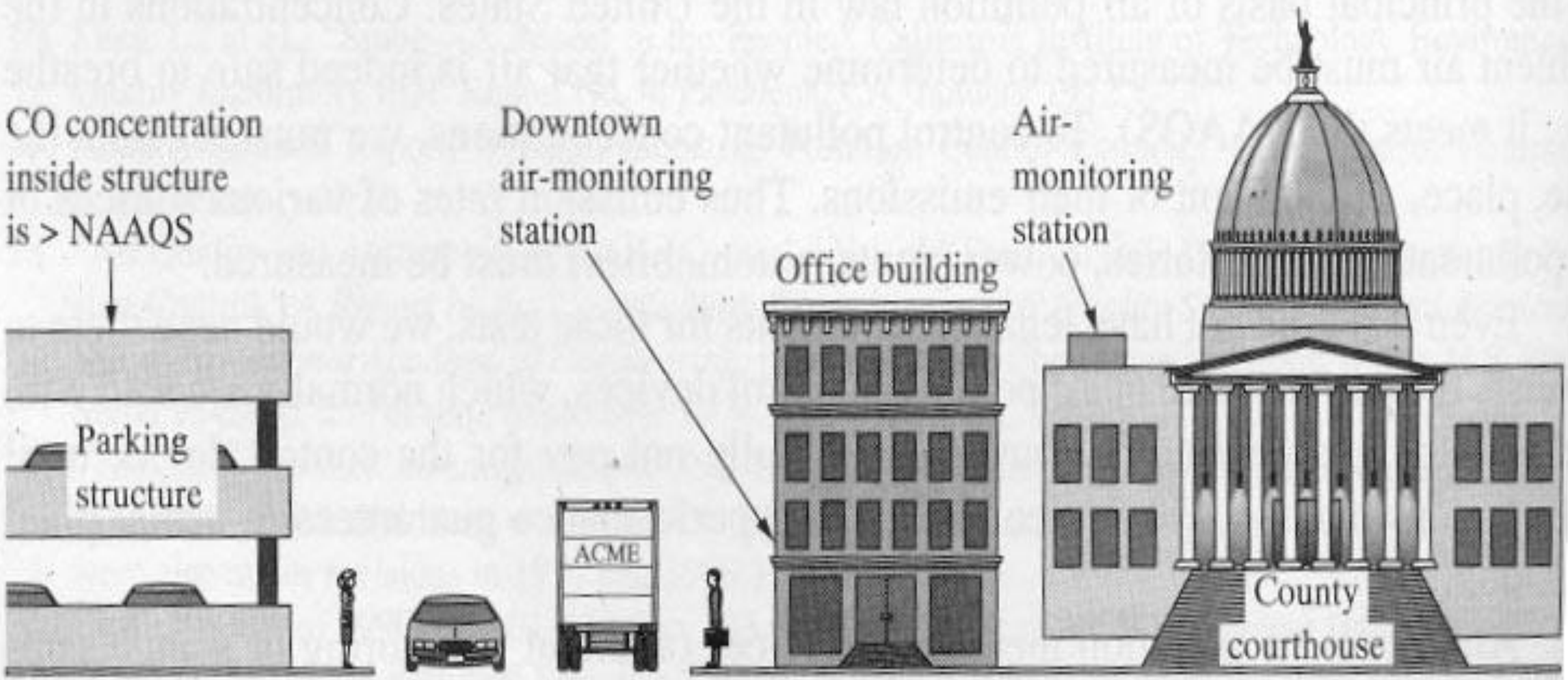


FIGURE 4.2
Illustration of some of the problems of choosing a sampler site to measure ambient CO in a city.

Figure 4.2 de Nevers

Samples

The sample is one of the critical elements of the analytical process. Why?

- Quality of any data produced by any analytical system primarily depends on the sample analyzed
- Sample must be representative of the whole so that the final result of the analysis represents the entire system that it is intended to represent

Sampling procedures

- Procedures differ depending on the samples of interest.
- It is very important that sampling and preservation protocols are adhered to closely.
- These are available in standard manuals and texts such as:
- Environmental Sampling and Analysis by Maria Csuros, 2/E 1997. Lewis Publishers.
- Fundamentals of environmental sampling and analysis by Chunlong Zhang, 2007.
- EPA Manuals, etc

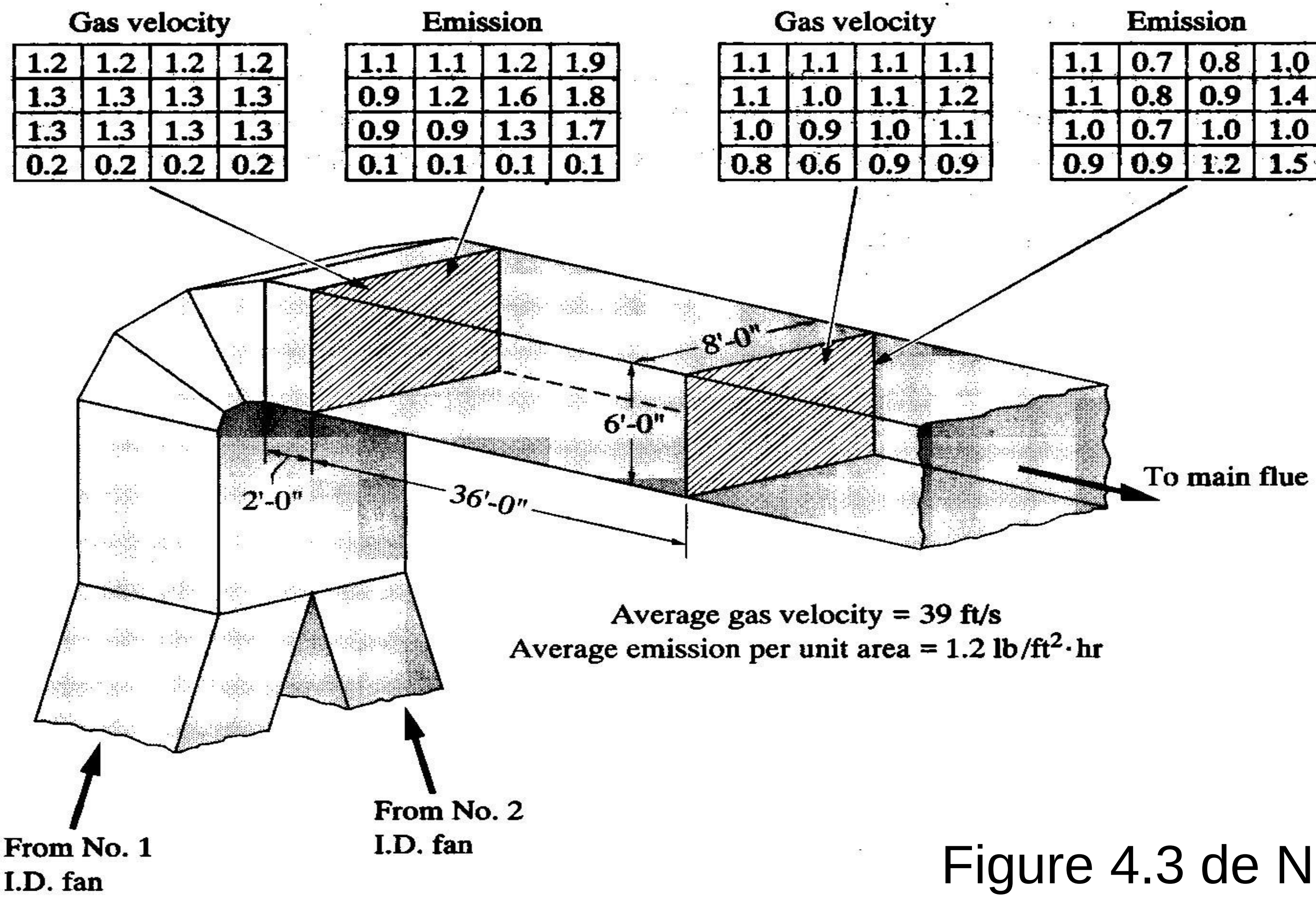


Figure 4.3 de Nevers

FIGURE 4.3
Measured velocities and particle mass flow rates (velocity × concentration) in a complex duct. The values shown are the ratio of the observed value to the average value for the whole duct. For example, near the bend, where the velocity is shown as 1.2, the measured velocity was 1.2×39 ft/s $= 47$ ft/s $= 14.3$ m/s [2].

Figure 4.5 de Nevers

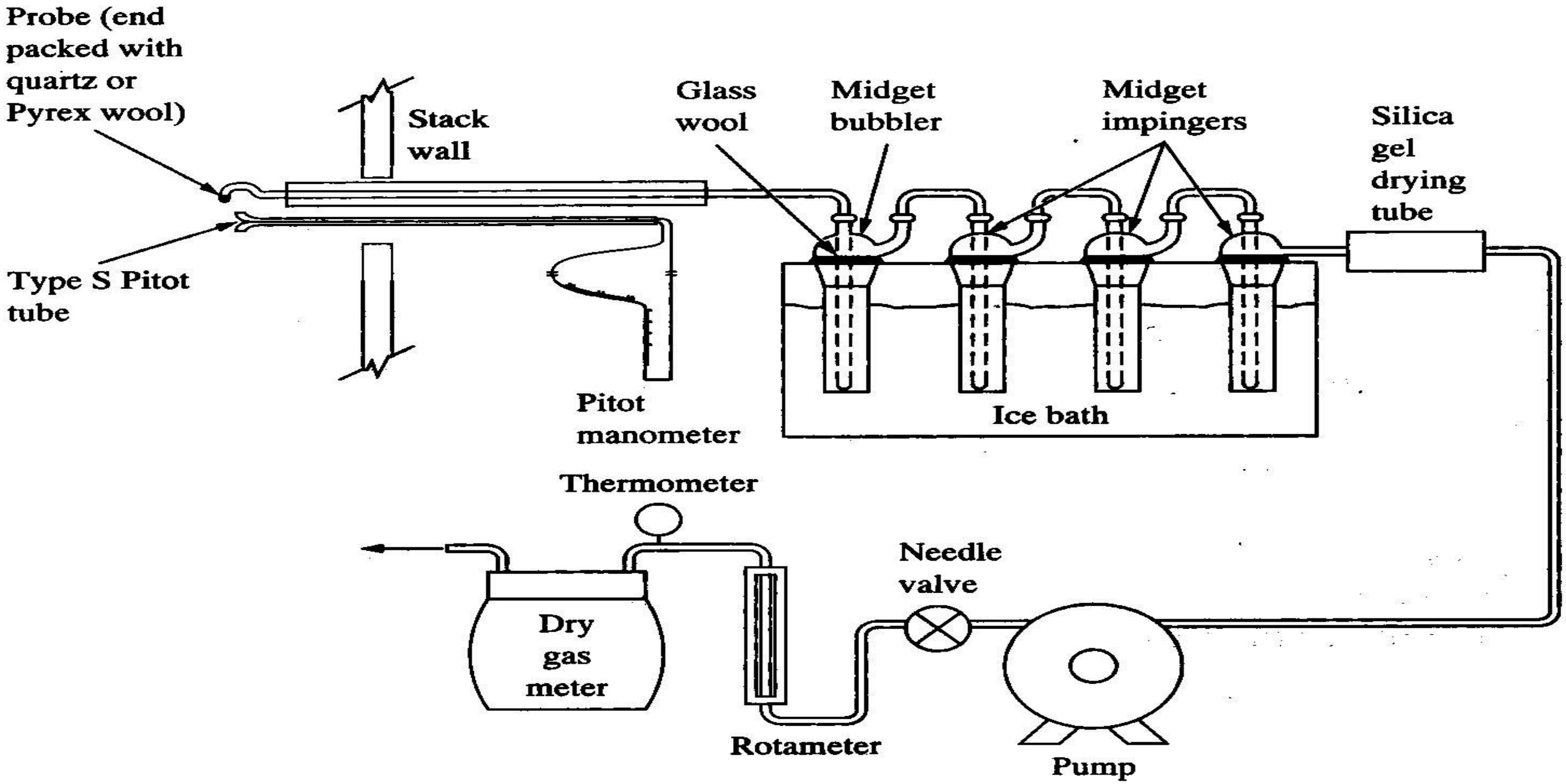


FIGURE 4.5
U.S. EPA "Method 6" sampling train for SO_2. Glass wool excludes particulate matter from the rest of the sampling train. The midget bubbler contains an aqueous isopropanol solution, which removes SO_3 but not SO_2, its contents are discarded after the sampling is completed. The first two midget impingers contain an aqueous solution of hydrogen peroxide; the third impinger is empty and traps carryover liquid from the second. At the end of the test, the contents of the three midget impingers, plus the water used to rinse them, are combined and titrated with barium perchlorate, using a thorin indicator. The silica gel drying tube protects the pump, rotameter, and dry gas meter from moisture carried over from the impingers [4].

Standard Analytical Methods

TABLE 4.1
Test methods for major air pollutants in ambient air

In EPA terminology, for each major air pollutant there is a *reference method*, which is the test method that is considered the standard against which other methods can be tested, and there are *equivalent methods*, which have been checked against the reference method and found to give similar results. State and local ambient monitoring agencies mostly use the equivalent methods, which are generally simpler, cheaper, and easier to use than the reference methods. This table lists only the reference methods. All of the material in this table is described in much more detail in Ref. 1.

Particulate Matter, TSP, PM_{10}, and $PM_{2.5}$. There are three standard methods. In all three a sample is drawn through an inlet designed to exclude particles larger than a certain size (50 μ, 10 μ, and 2.5 μ, respectively), and then collected on a filter for 24 hours. The filter's gain in weight is divided by the measured cumulative air flow through the filter to determine the particle concentration (see Example 4.2). The filter size and air flow are much larger for the TSP and PM_{10} devices than for the $PM_{2.5}$ device. The TSP (total suspended particulate) filter is used only for the lead measurement, described below. Both PM_{10} and $PM_{2.5}$ are used to test compliance with the applicable NAAQS.

Sulfur Dioxide (SO_2). In the West-Gaeke method a known volume of air is bubbled through a solution of sodium tetrachloromercurate, which forms a complex with SO_2. After several intermediate reactions, the solution is treated with pararosaniline to form the intensely colored pararosaniline methyl sulfonic acid, whose concentration is determined in a colorimeter.

Ozone (O_3). The air is mixed with ethylene, which reacts with ozone in a light-emitting (chemiluminescent) reaction. The light is measured with a photomultiplier tube.

Carbon Monoxide (CO). The concentration is measured by nondispersive infrared (NDIR) absorption. Here *nondispersive* means that the infrared radiation is not dispersed by a prism or grating into specific wavelengths; rather, filters are used to obtain a wavelength band at which CO strongly absorbs.

Hydrocarbons (Nonmethane). The test is for hydrocarbons excluding methane. The gas is passed through a flame ionization detector (FID), where the hydrocarbons burn in a hydrogen flame. Hydrocarbons cause more ionization than hydrogen; this ionization is detected electronically. Part of the sample is diverted to a gas chromatograph, where methane is separated from the other gases and then quantified. Its concentration is subtracted from the total hydrocarbon value from the FID. Although there is no NAAQS for hydrocarbons, its measurement in ambient air is required as part of the control program for O_3, for which it is a precursor.

Nitrogen Dioxide (NO_2). NO_2 is converted to NO, which is then reacted with ozone. The light from this chemiluminescent reaction is measured. Because ambient air contains NO (often more than NO_2), a parallel sample is run without conversion of the NO_2 to NO, and the resulting NO reading is subtracted from the combined NO and NO_2 reading to give the NO_2 value. The instrument normally reports the NO concentration as well.

Lead. A TSP filter is extracted with nitric and hydrochloric acids to dissolve the lead. Atomic absorption spectroscopy is then used to determine the amount of lead in the extract.

Federal Reference Methods for Criteria Pollutants

Pollutant	Reference Method
SO_2	Spectrophotometry (para-rosanilne method)
NO_2	Gas-phase chemiluminescence
CO	Nondispersive infrared photometry
O_3	Chemiluminescence
NMHCs	Gas chromatography – FID (flame ionization detection)
PM_{10}	Performance-approved product
$PM_{2.5}$	Performance-approved product

Particulate Pollutants

PM_{10} sampler with size-selective inlet

http://www.recetox.muni.cz/images/airsag/PM10.jpg

- Impaction and filtration are the primary PM collection principles
- Measure the weight of exposed and clean filters
- High-volume sampler (Hi-Vol)
- Typical sampling duration – 24 h

PM_{10} Sampler

- Remove particles > 10 µm by impaction on a greased surface
- Particles < 10 µm collected on a quartz glass fiber filter

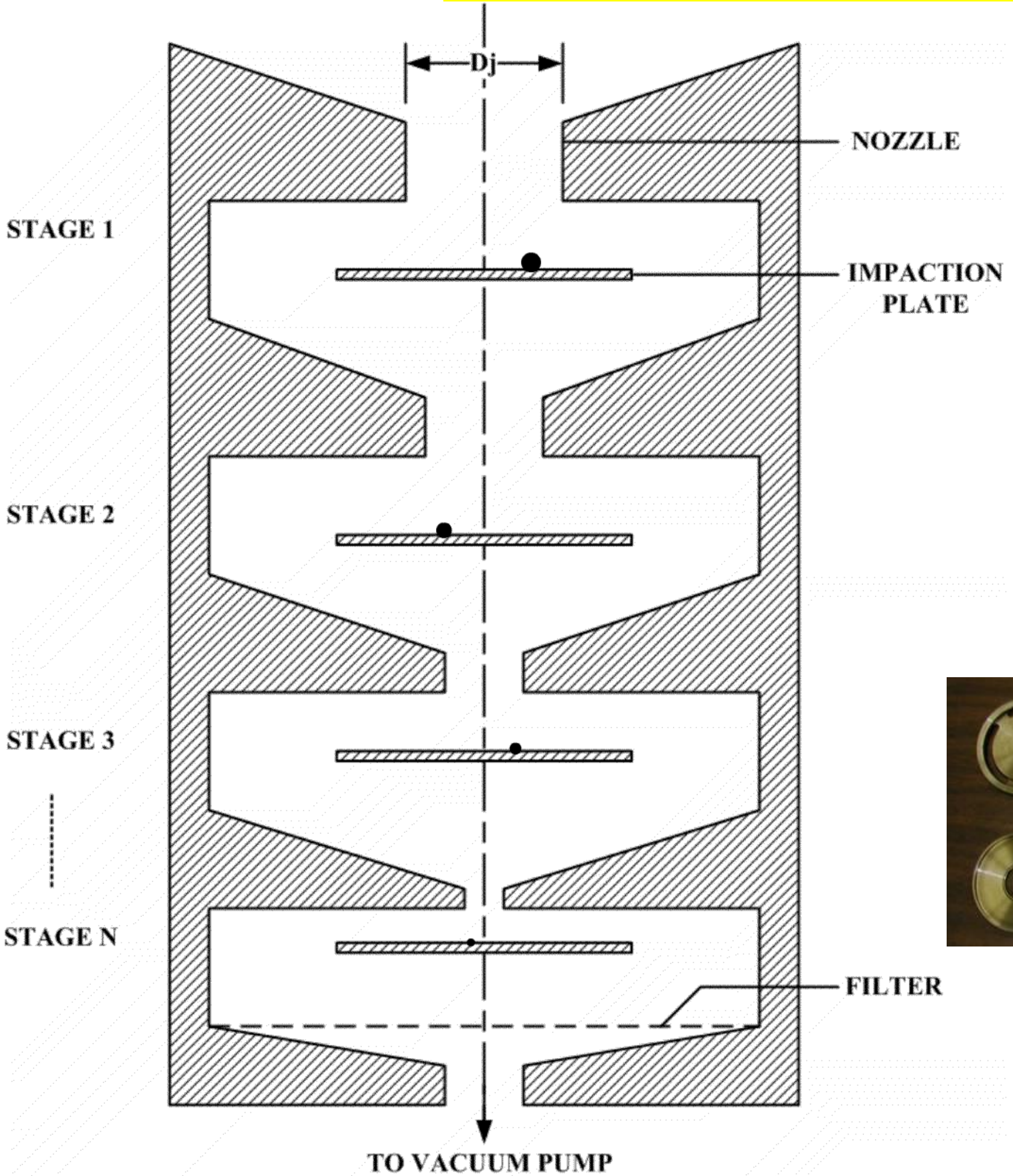
What does the PM_{10} sampler measure? Number or mass concentration of particles?

Hi-Vol Sampler

- Accepts particles 25-50 μm in size.
- Volume of air ~200 m^3 over 24 hours or week, etc.
- The filters used are usually glass fibres with a collection efficiency of ~99% for particles 0.3 μm in diameter.
- The technique is for determining the total levels of particulate matter.
- Can have PM_{10} and $PM_{2.5}$ samplers. These will sample for particles with aerodynamic diameters of 10 (or 2.5) μm or less.

Animation – Cascade Impactor

Cascade Impactor



Aerosol flow In

Clean air out

Particulate Matter

Particle samples are collected by filtration and impactors.

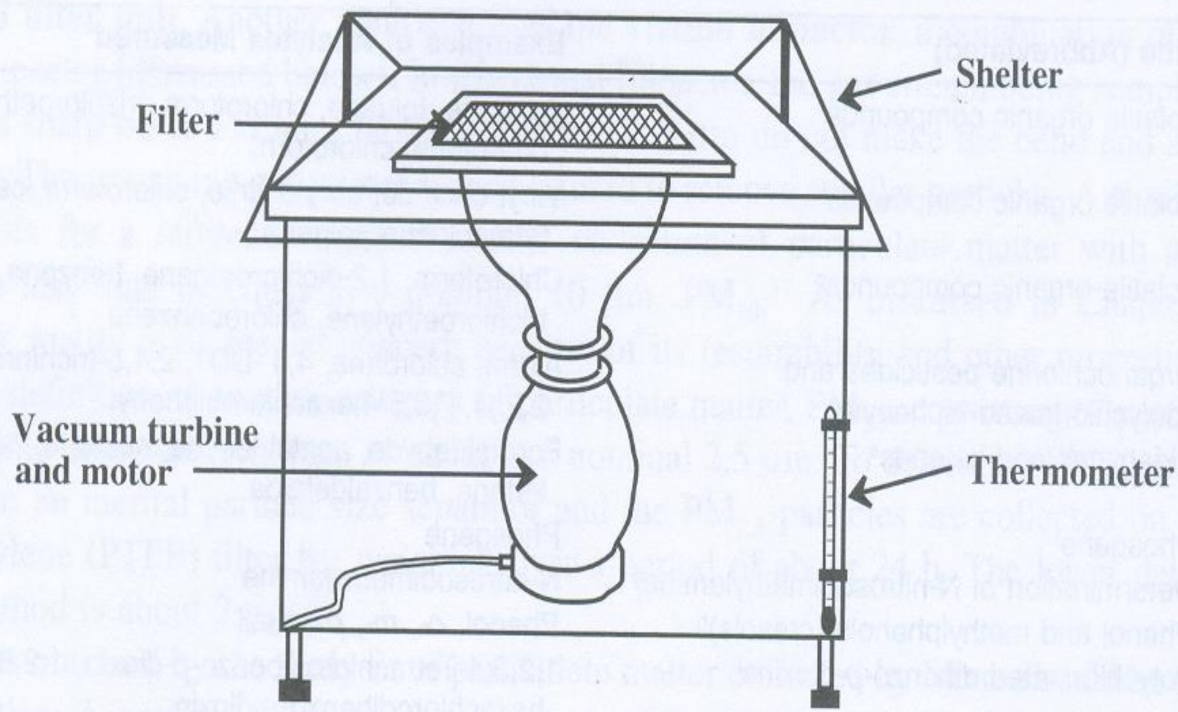


Figure 26.5 Hi-Vol sampler for the collection of particulate matter from the atmosphere for analysis.

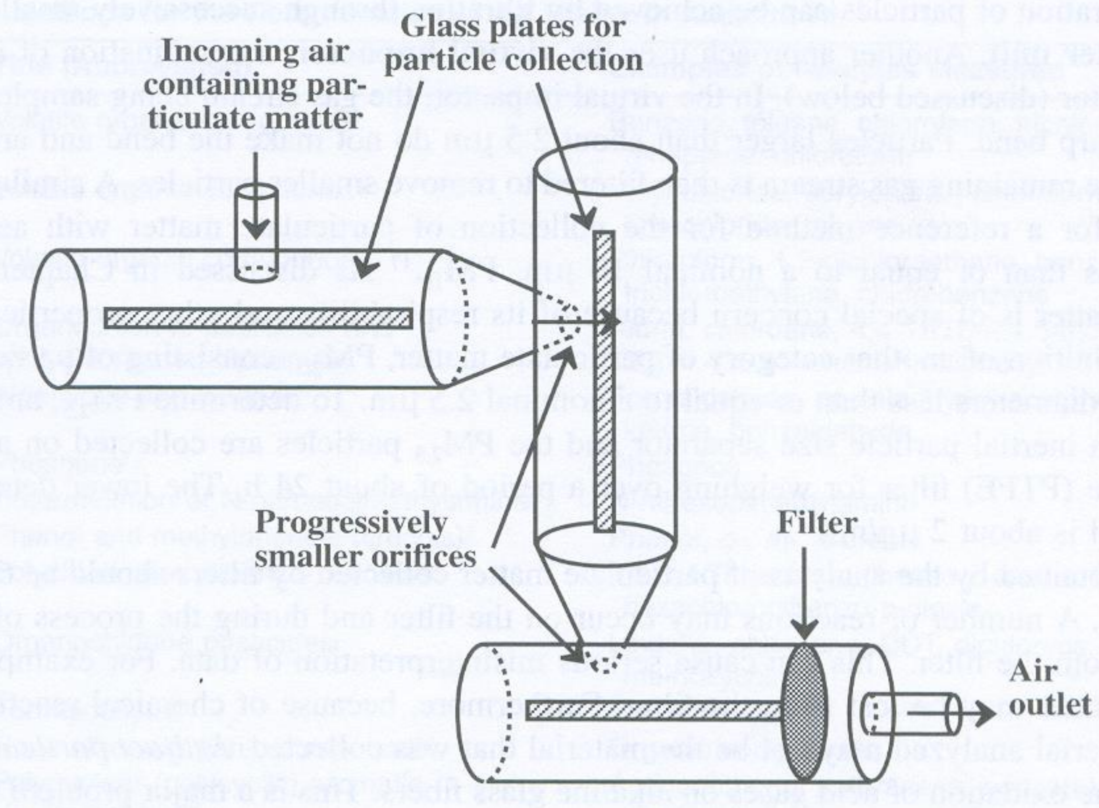


Figure 26.6 Schematic representation of a cascade impactor for the collection of progressively smaller particles.

Collection by Impactors

Impactors cause a relatively high velocity gas stream to undergo a sharp bend such that particles are collected on a surface impacted by the stream.

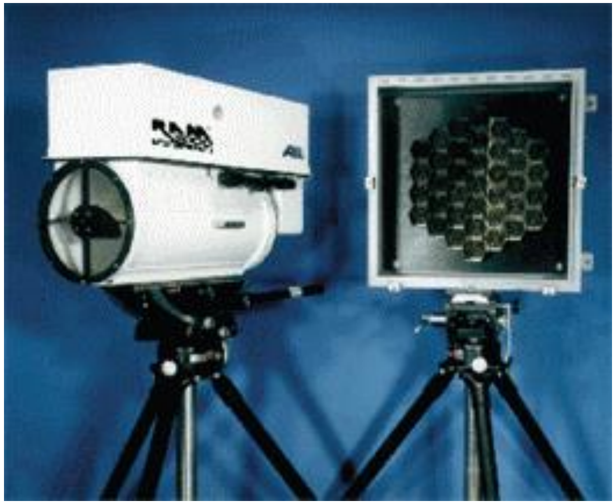
SO_2

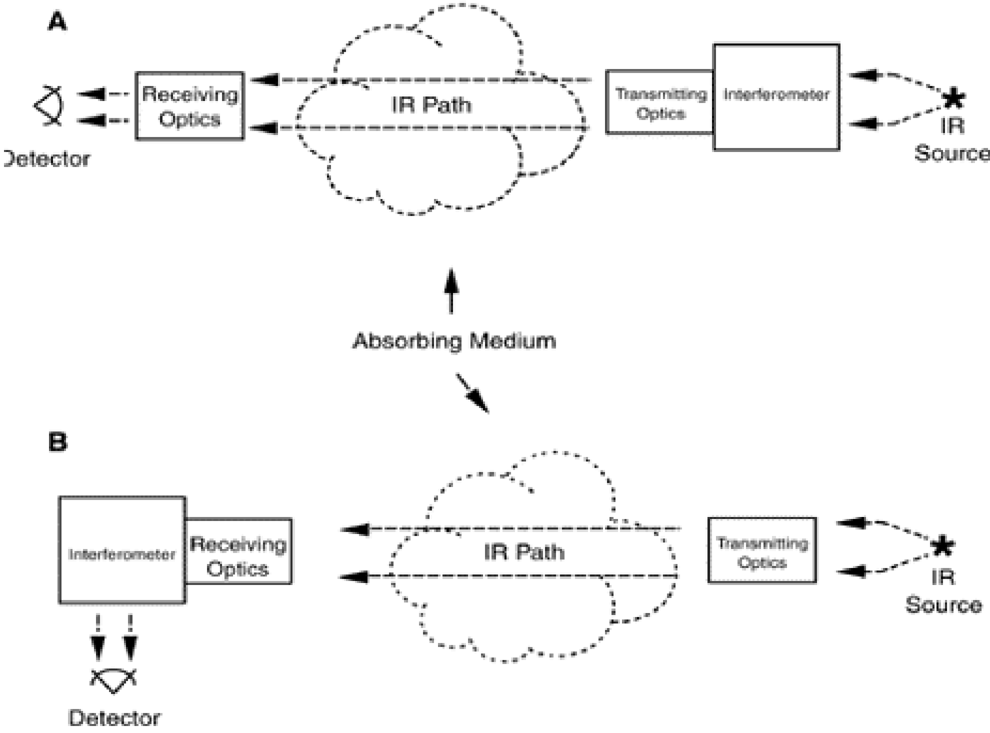
FRM* - Spectrophotometry (pararosanilne method)

Air sample → potassium tetrachloromercurate solution → $HgCl_2SO_3^{-2}$ → react with HCHO and colorless pararosaniline hydrochloride → red-violet product → measured spectrophotometrically → SO_2 concentration

EM* – FT- IR Spectrometry

(Absorption of IR by SO_2 in the air → SO_2 concentration)





http://clu-in.org/programs/21m2/openpath/op-ftir/images/exhibit3.gif

* **FRM**: Federal Reference Method **EM**: Equivalent Method

SO_2

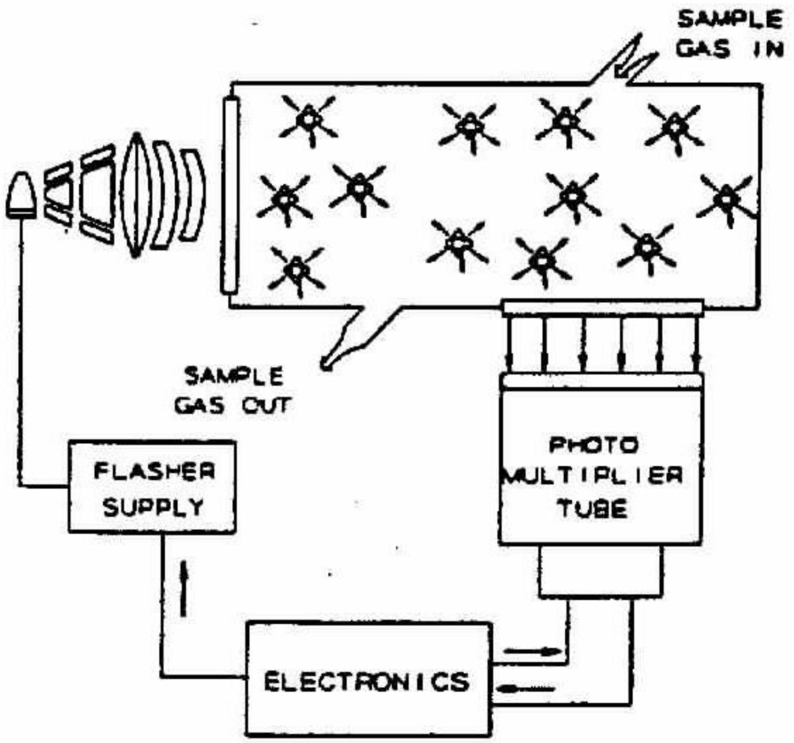
EM – UV Fluorescence

1) UV light excites SO_2 to a higher energy state

$SO_2 + hv_1 \rightarrow SO_2^*$

2) Decay of the excited SO_2^*, emitting a characteristic radiation

$SO_2^* \rightarrow SO_2 + hv_2$



www.cse.polyu.edu.hk/~airlab/so2.jpg

NO – NO_2 – NOx

FRM – Gas-Phase Chemiluminescence

Chemiluminescence: emission of light from electronically excited chemical species formed in chemical reactions.

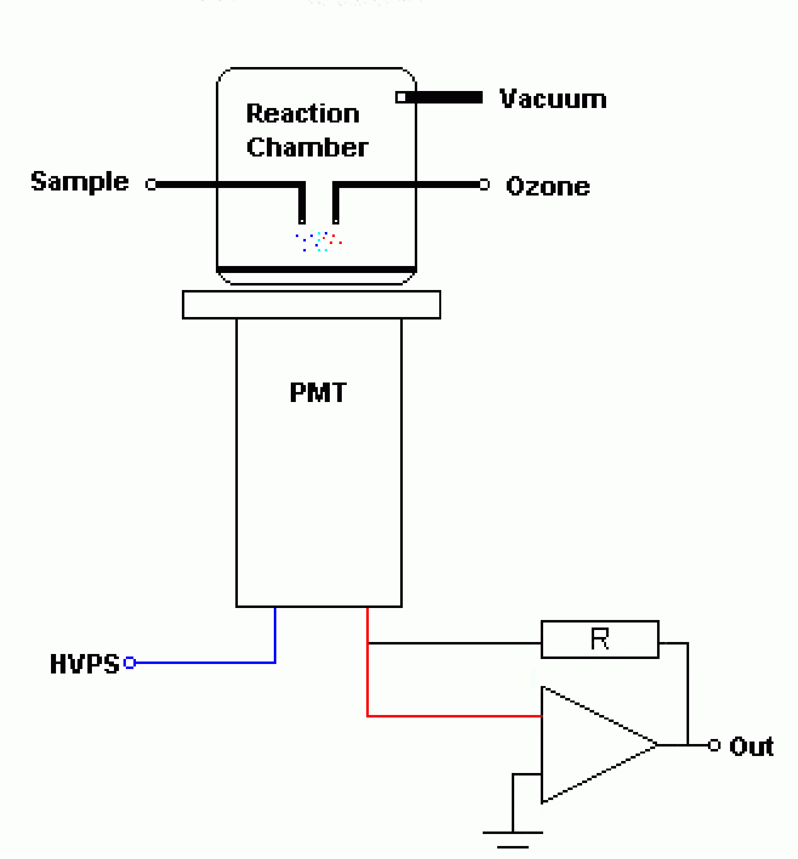
$NO + O_3 \rightarrow NO_2^* + O_2$

$NO_2^* \rightarrow NO_2 + h\nu$

Measurement of NO_2: conversion of NO_2 to NO, and subsequent measurement by chemiluminescence.

$2NO_2 + Mo \rightarrow 3\ NO + MoO_3$

Possible interference: N-containing compounds → higher measured NO_2



EM – FT- IR Spectrometry

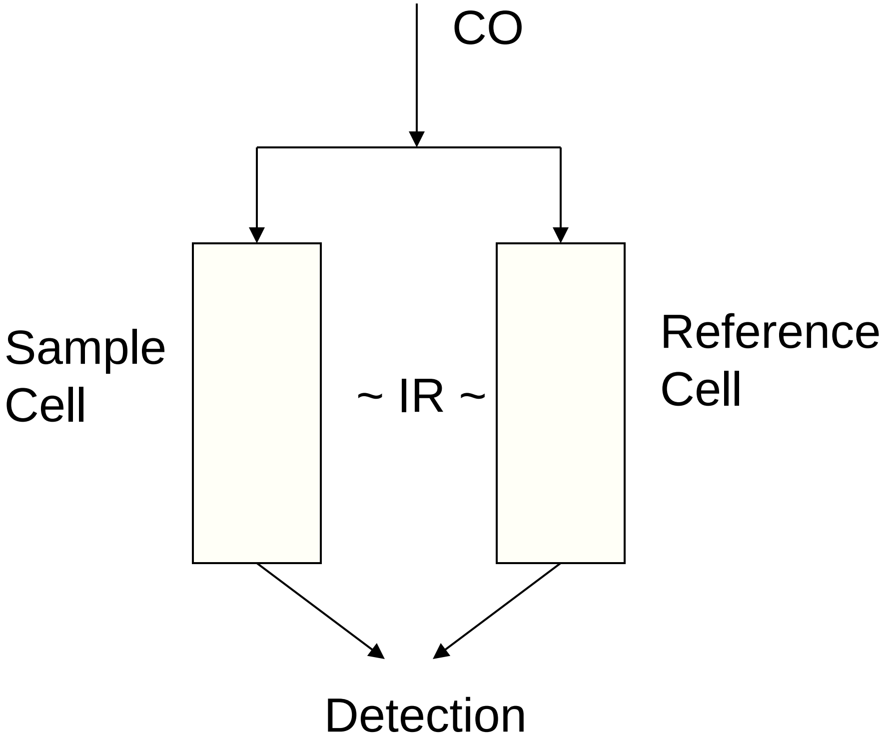
www.k2bw.com/images/chem.gif

CO

FRM – **Nondispersive Infrared (NDIR) spectrometry**

CO strongly absorbs infrared energy at certain wavelengths.

Detection device: two cylindrical cells, a sample and a reference cell.
Difference in infrared energy in the two cells → concentration of CO



O_3

FRM – Chemiluminescence

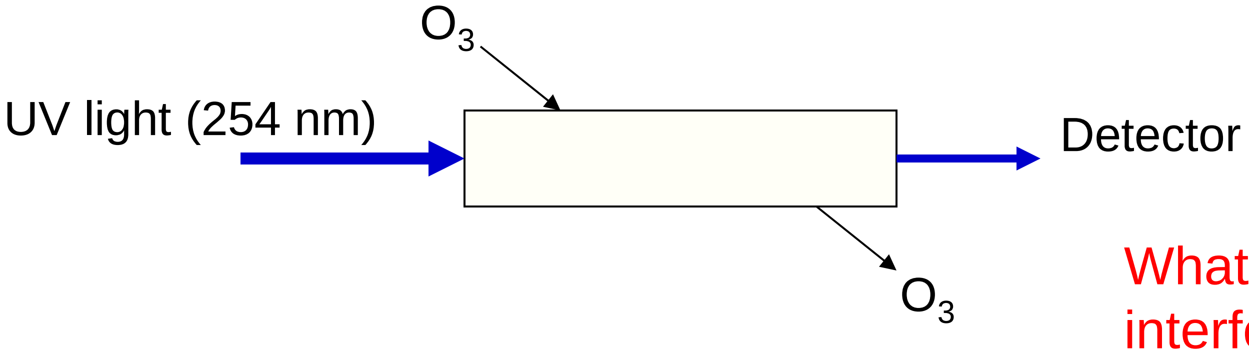
Light emissions produced on reaction of O_3 with ethylene (C_2H_4).

C_2H_4 flammable – replaced by Rhodamine B dye embedded in a disk

Rhodamine B does not attain a stable baseline rapidly after exposure to O_3

EM – UV Photometry

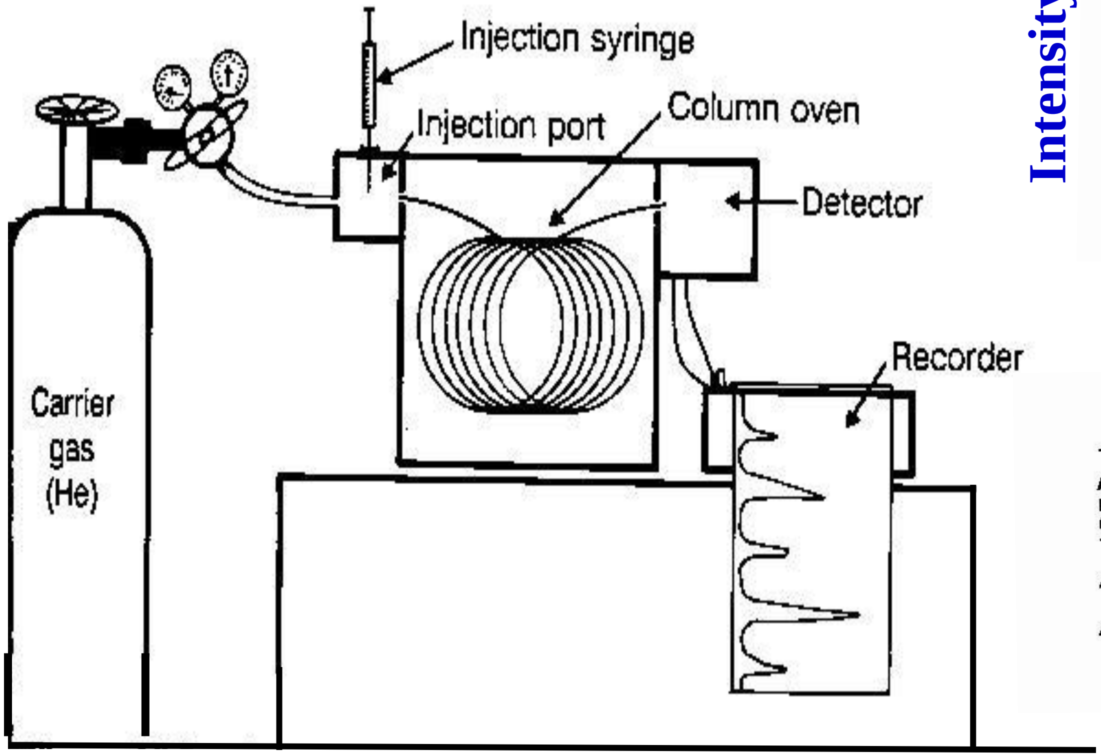
Absorption of UV light (254 nm) by O_3 and subsequent use of photometry to measure the reduction of UV energy

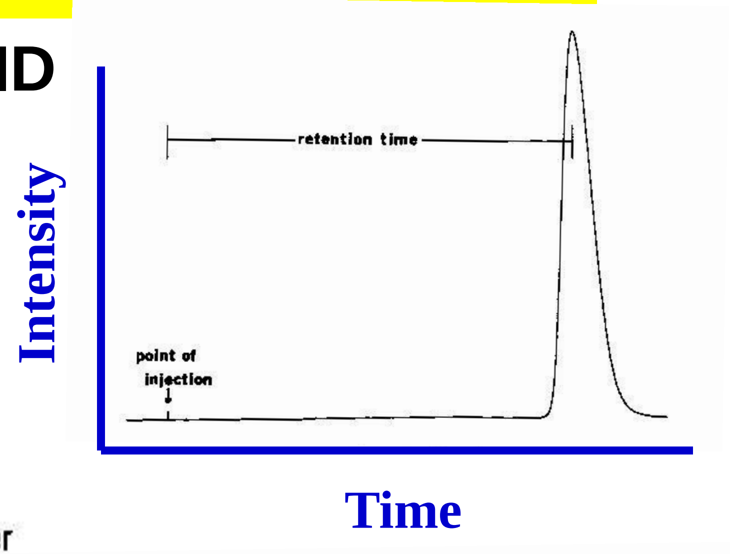


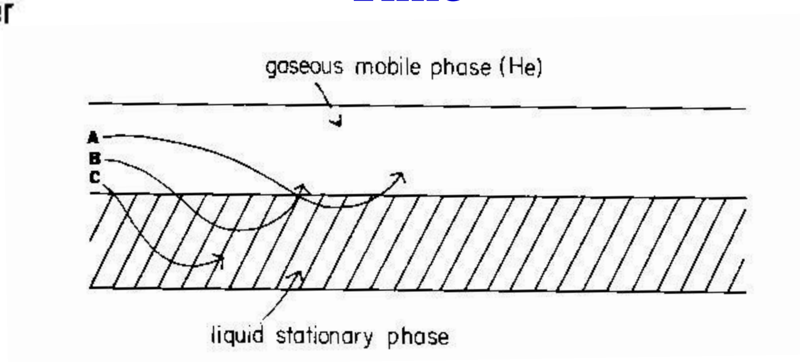
What would cause an interference on a UV photometry O_3 monitor?

NMHCs

FRM – Gas Chromatography - FID







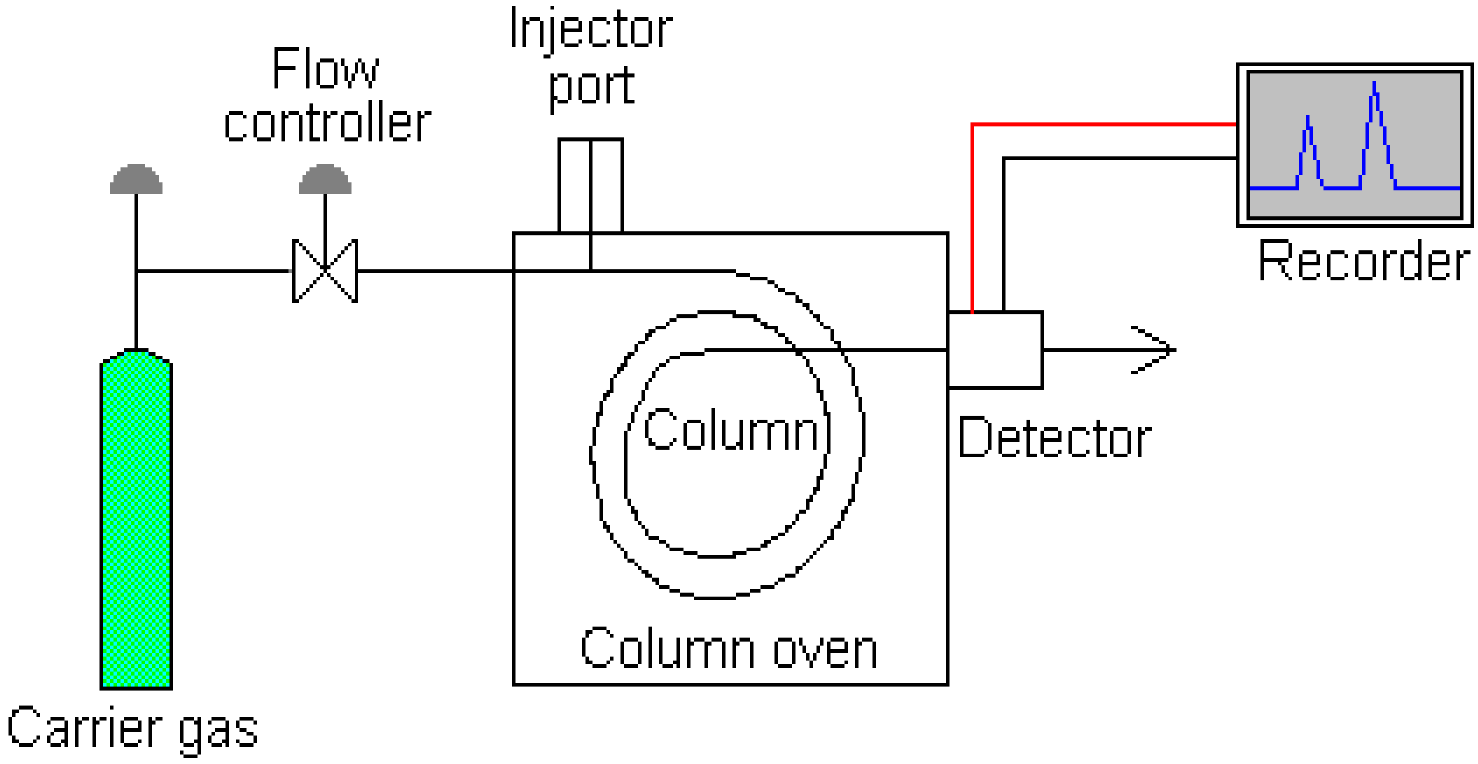
Stationary and mobile phases

GC-Detector:

Generate an electronic signal when a gas other than the carrier gas elutes from the column.

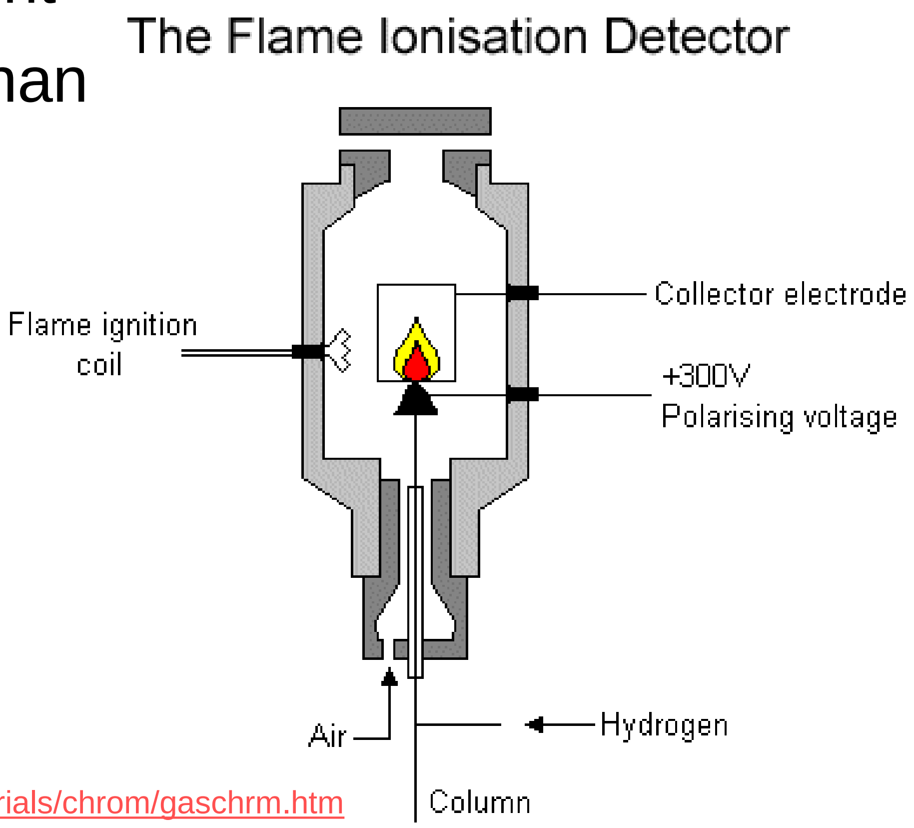
Gas Chromatography (GC)

GC is an instrumental method for the separation and identification of chemical compounds.



NMHC

- FID – Flame Ionization Detection:
  - Combustion of organic substances
  - Positive ions (+) and electrons (-) are formed when burned – change in current
    - Mass sensitive rather than concentration sensitive



http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

Ozone

- Colorless gas with a pungent, irritating odor
- Continuously monitored with analyzers that measure the amount of UV absorbed by molecular ozone
- Sampling Method (Ultraviolet Photometry)
- Equivalent Method
- Analyzers
  - UV Analyzers
  - Mercury lamp (UV Source)
  - Analytical wavelength = 254 nm
- Dasibi 1003AH
- API 400

Carbon Monoxide

- Colorless, odorless gas
- Continuously monitored with analyzers that take advantage of its strong tendency to absorb IR radiation
- Sampling Method (Non-Dispersive Infared Radiation, NDIR)
- Reference Method
- Analyzers
  - NDIR
  - Gas Filter Correlation
  - Analytical wavelength 4.7 μm
- TECO 48
- Dasibi 3008

Nitrogen Dioxide

- Reddish-brown gas, with irritating odor
- Continuously monitored indirectly with analyzers that measure total oxides of nitrogen
- Sampling Method (Gas Phase Chemiluminescence)
- Reference Method
- Analyzers
  - Chemiluminescence
  - $NO + O_3 \longrightarrow NO_2 + h\nu$ (300 - 500 nm)
  - High energy to generate O_3
  - Directly measure NO only
  - Reduce NO_2 to NO in converter
  - Measure total NO_x
  - Calculate NO_2 by difference (NOx - NO)
- TECO 14B and TECO 42

Sulfur Dioxide

- Colorless gas, with a strong suffocating odor
- Continuously monitored with analyzers that measure the level of fluorescence emitted by SO2 after being exposed to UV light
- Sampling Method (UV Fluorescence)
- Equivalent Method
- Analyzers
  - Fluorescence analyzers
  - UV excitation light (210 nm)
  - Measure emitted light (350 nm)
- TECO 43

Source Sampling and Monitoring

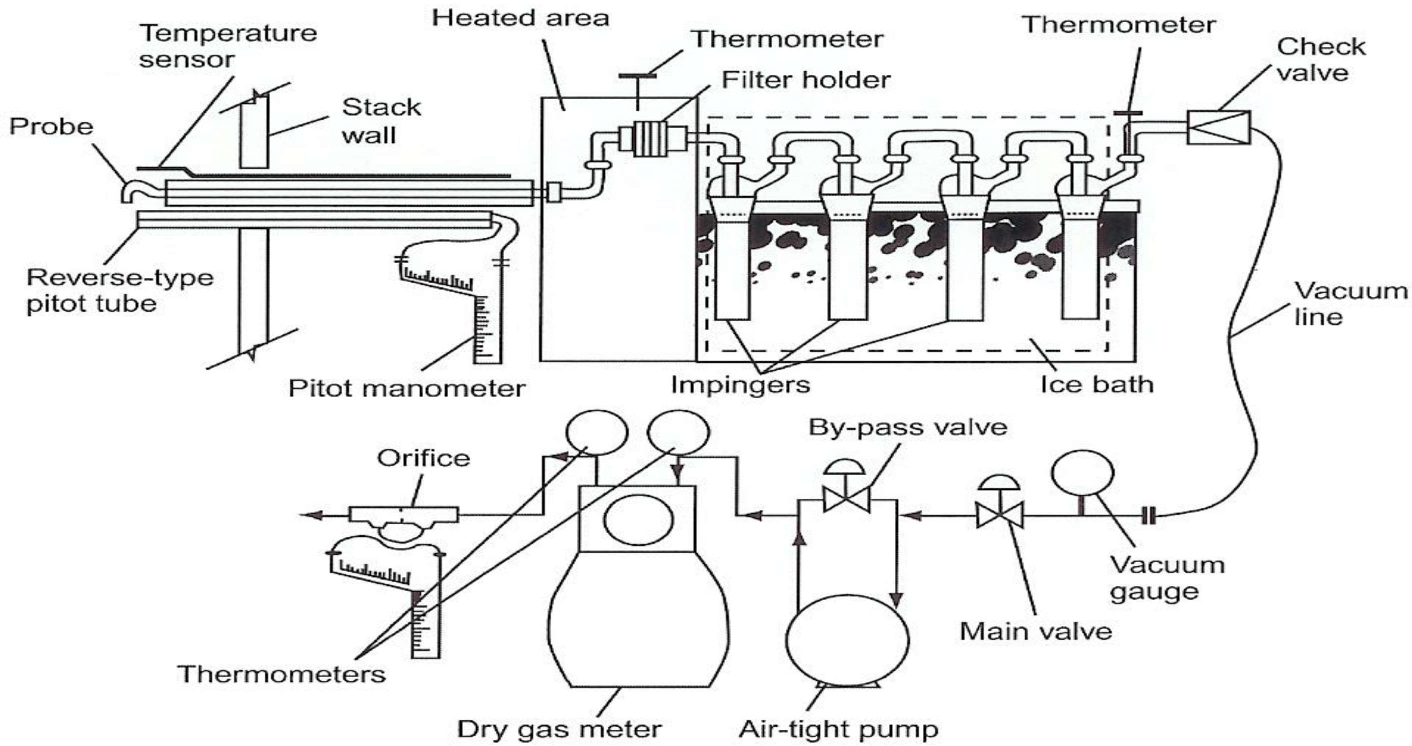


Figure 7.9 USEPA reference method for PM stack sampling. (From CFR 40, Part 60, Appendix 5, Method 5, p. 625, July 1, 1989.)

Stack Sampling of PM

1) Probe inserted into the stack
2) Temperature sensor
3) Pitot tube – gas velocity and flow rate
4) Two-module sampling unit

Isokinetic Sampling

1) Particles – inertial forces
2) Samples must be collected at the same rate of low as the stack gas

DETERMINING POLLUTANT FLOW RATES

The mass flow rate of pollutant is the product of the concentration in the gas and the molar or mass flow rate of the gas, e.g.,

Pollutant molar flow rate = (molar flow rate of gas) x (pollutant molar concentration in gas)

(de Nevers, p.72)

Example 4.3.

The sampling train shown in Fig. 4.5 indicates that the concentration of SO_2 in a stack is 600 ppm. The Pitot tube and manometer in the same figure indicate that the flow velocity is 40 ft/s. The stack diameter is 5 ft. The stack gas temperature and pressure are 450° F and 1 atm. What is the SO_2 flow rate?

(de Nevers, p.71)

Air Monitoring Station

Air Monitoring Instrumentation

Monitoring Objectives

- To determine highest concentrations expected to occur in the area covered by network
- To determine representative concentrations in areas of high population density
- To determine impact on ambient pollution levels of significant source categories
- To determine background concentration levels

Scales of Monitoring

1. Urban
   – Concentrations in air volumes from 4 to 50 Km

2. Regional
   – Concentrations in rural air volumes from tens to hundreds of Km

3. National and Global
   – Concentrations in air volumes from representing a nation or the world as a whole

Monitoring Considerations

1. Sampling location: limited number of fixed site monitors whose locations reflect objectives of air quality monitoring program

   What are the objectives?

   Examples of criteria for selecting ambient sampling locations?

2. Lower limit of detection (LOD): a sufficient amount of pollutant must be collected, f(sampling rate, duration)
   - Integrated sampling vs. real-time sampling
   - Area sampling vs. personal sampling
3. Collection efficiency of the instrument:
   - Low flow rate for gas-phase contaminants (< 1 L/min)

Calibration

- Often used for adjusting **bias-type** errors
- Measured values are compared to standard reference values (for pollutant concentration) or standard airflow measuring techniques/devices (for volume air flow)
- **Primary** vs. **secondary** standard for flow: traceable to the National Institute of Standards and Technology (NIST)
  - Primary: bubble meter
  - Secondary: wet or dry test meters calibrated by bubble meter
- Gas standards: traceable to a NIST reference material
  - CO, SO_2, NO_2, NO: available in cylinder gas or permeation tubes
  - O_3: NIST certified O_3 generator

Quality Assurance Programs

Goal: Valid and reliable air quality monitoring data

Quality Assurance (QA)

- Setting policy and overseeing management controls
- Planning, review of data collection activities and data use
- Setting data quality objectives, assigning responsibilities, conducting reviews, and implementing corrective actions

Quality Control (QC)

- Technical aspects of data quality programs
- Implementation of specific QC procedures: calibrations, checks, replicate samples, routine self-assessment, and audits

Accuracy, Precision and Bias

Relative Error: $E_r(\%) = \frac{O - A}{A} \times 100$ → **Bias**

Coefficient of variation: $CV(\%) = \frac{\sigma}{\bar{X}} \times 100$ → **Precision**

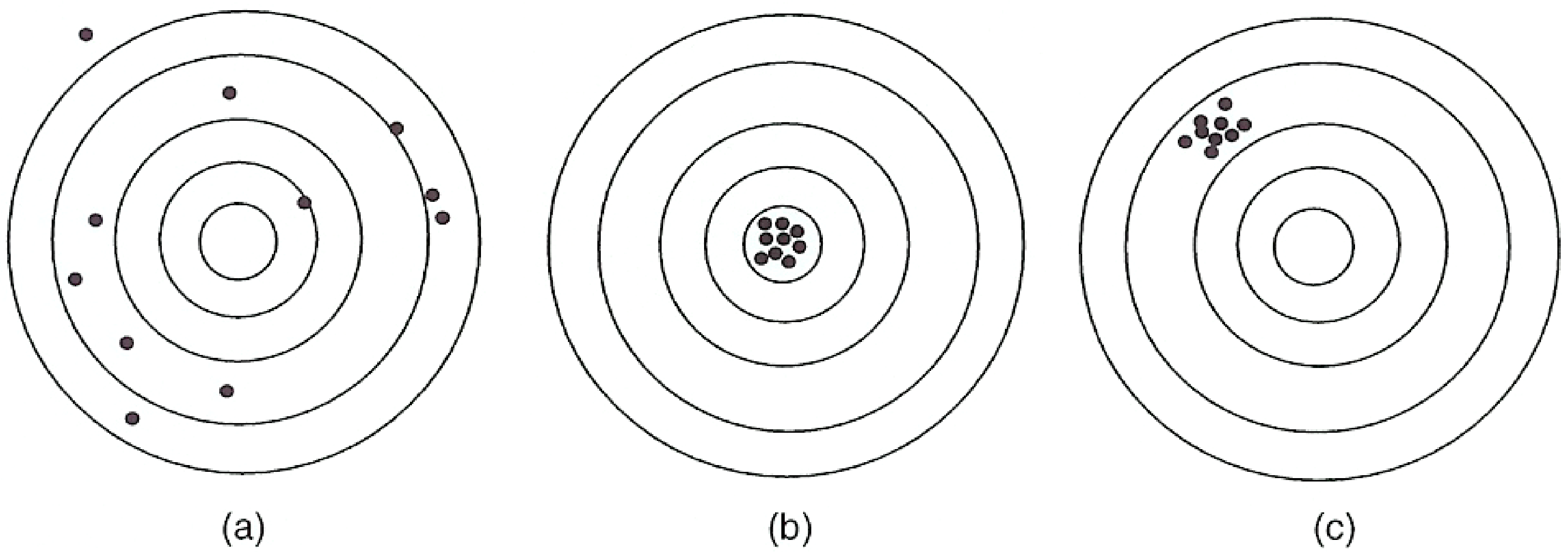


Figure 7.5 Graphical illustration of accuracy, precision, and bias.

Accuracy is a combination of random (precision) & systematic (bias) errors. Which of the 3 cases has the highest accuracy? Why?

Air Quality Index

- The Air Quality Index (AQI) is an indicator of air quality, based on hourly pollutant measurements of some or all of the six most common air pollutants: Sulfur dioxide, ozone, nitrogen dioxide, total reduced sulfur compounds, carbon monoxide and fine particulate matter.
- Several state-of-the-art air monitoring stations, operated by MOE,form the Air Quality Index (AQI) network

(Canadian experience).

AQI (continued)

- If the air quality value is below 32, the air quality is considered relatively good.
- If the AQI value is in the range of 32 to 49 (moderate category), there may be some adverse effects on very sensitive people.
- An index value in the 50 to 99 range (poor category), may have some short-term adverse effects on the human or animal populations, or may cause significant damage to vegetation and property.
- An AQI value of 100 or more (very poor category) may cause adverse effects on a large proportion of those exposed.

Air Quality index, AQI

- an indicator of air quality, based on hourly pollutant measurements of some or all of the six most common air pollutants: SO_2, O_3, NO_2, TRS, CO, $PM_{2.5}$

0 – 32	Good
32 – 49	Moderate
49 – 99	Poor
99 <	Very poor

- At the end of each hour, the concentration of each pollutant that the AQI station monitors is converted into an AQI sub-index. The pollutant with the highest sub-index defines AQI.

Quality Assurance Programs

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Air Monitoring Instrumentation

- Gaseous
  - Ozone, CO, NO_x, HC, SO_2
- Meteorological Instruments
- Particulate
- Toxics
- Calibration Instrumentation

Monitoring Equipment