

## Sub Module 4.3

### Gas concentration measurement

#### **Introduction:**

In recent times there is a lot of concern regarding the presence and the concentration levels of harmful gases in the earth's atmosphere. Quantitative analysis of these is important from these as well as other considerations. Monitoring the health of a power plant requires the monitoring the levels of various gases in the gases that leave through the stack. In the case of internal combustion engines the analysis of the exhaust leaving through the tail pipe of a car provides important information about the performance of the engine. In view of these we look at the following in what follows:

- a) Flue gas monitoring
- b) Atmospheric pollution monitoring
- c) Exhaust gas analysis in IC Engines

However, before we embark on these we shall look at ways of specifying the concentration of gases. The concentration of a candidate gas in a mixture of gases may either be specified on volume basis or on mass basis. On volume basis the units are either ppm<sub>v</sub> (parts per million) or ppb<sub>v</sub> (parts per billion). For example, a ppm of gas on volume basis is defined as

$$1 \text{ ppm}_v = \frac{\text{Volume of candidate gas}}{\text{Total volume of gas mixture}} \times \frac{1}{10^6} \quad (33)$$

Gas concentration in ppb is given by

$$1 \text{ ppb}_v = \frac{\text{Volume of candidate gas}}{\text{Total volume of gas mixture}} \times \frac{1}{10^9} \quad (34)$$

Note that 1 ppm is also equal to 0.0001% by volume.

On mass basis the units normally employed are  $\text{g/m}^3$  or  $\text{mg/m}^3$ . This means that 1 mg of the candidate gas is present in a cubic meter of the gas mixture. The unit also represents the density of the candidate gas per unit volume of the gas mixture. In many applications the volume may simply be taken as the volume of all the other gases put together since the concentration of the candidate gas is very small or required to be very small. It is possible to convert concentration from volume basis to mass basis by the use of gas laws applied to mixture of gases. We assume that the gas mixture is mostly standard dry air with a small concentration of the candidate gas. Let the density of the candidate gas in the mixture be  $\rho_c$ , given in  $\text{mg/m}^3$ . Let the total pressure be one standard atmosphere equal to  $P = 101325 \text{ Pa}$ . Let the temperature of the gas mixture be  $T \text{ K}$ . The universal gas constant is given by  $R = 8314.47 \text{ J/Mol K}$ . The partial pressure of the candidate gas is then given by  $p_c = \rho_c \frac{RT}{M_c}$  where  $M_c$  is the molecular weight of the candidate gas. The total gas pressure is given by  $P = \rho \frac{RT}{M}$  where  $M$  is the molecular weight of air. The ratio of partial pressures is the same as the ratio of volumes and is given by division of these two expressions as

$$\frac{p_c}{P} = \frac{V_c}{V} = \frac{\rho_c}{\rho} \frac{M}{M_c} = \frac{\rho_c}{M_c} \frac{M}{\rho} = \frac{\rho_c}{M_c} \frac{RT}{P} \quad (35)$$

If the candidate density is specified in  $\text{mg/m}^3$ , the above may be simplified to

$$\begin{aligned} \frac{V_c}{V} &= \frac{\rho_c}{M_c} \frac{RT}{P} = \frac{1\text{mg}/\text{m}^3}{M_c} \frac{8314.47\text{J}/\text{kg K} \times T}{101325\text{Pa}} \\ &= \frac{8314.47}{101325} \times 10^{-6} \times \frac{T}{M_c} = \frac{T}{12.185 \times M_c} \text{ ppm} \end{aligned} \quad (36)$$

Note that the above is strictly valid for small amount of the candidate gas being present in the mixture.

\*(Fig 34, Table 2, and Example 10)

### Example 10

Gaseous pollutant  $\text{NO}_2$  has a mass concentration of  $20 \text{ mg/m}^3$  in an air sample at  $30^\circ\text{C}$  and at 1 atmosphere. Express this in ppm by volume basis.

The temperature of the gas sample is given as  $T = 30^\circ\text{C} = 273 + 30 = 303 \text{ K}$

Molecular weight of  $\text{NO}_2$  is  $M_c = 46.01$

Using Equation 36 we may represent the concentration in volume basis as

$$ppm_v = \frac{303}{12.185 \times 46.01} \times 20 = 10.81$$

### Example 11

Air sample at  $25^\circ\text{C}$  has 2.5 ppm by volume of  $\text{SO}_2$ . What is the concentration on mass basis?

The temperature of the gas sample is given as  $T = 25^\circ\text{C} = 273 + 25 = 298 \text{ K}$

Molecular weight of  $\text{SO}_2$  is  $M_c = 64$

The mass concentration in  $\text{mg/m}^3$  is given by

$$\rho_c = \frac{12.185 \times 64}{298} \times 2.5 = 6.5423 \text{ ppm}_v$$

Table 2 shows the mass concentration corresponding 1 ppm<sub>v</sub> of some candidate gases present in trace amounts.

Sometimes the pollutant concentrations are given in more appropriate units with certain applications in mind. For example pollutant levels in the case of automobile exhaust are specified in g/km.

### Combustion products commonly met with are:

- Oxides of Carbon – CO and CO<sub>2</sub>
- Oxides of Nitrogen – NO, N<sub>2</sub>O, NO<sub>2</sub> etc.
  - Referred to collectively as NO<sub>x</sub>
- Un burnt Fuel (HC)
- Particulate matter – Soot

Table 3 gives emission limits of combustion products commonly met with in exhaust gases from internal combustion engines.

**Table 2 Mass concentration in  $\mu\text{g}/\text{m}^3$  of 1 ppm<sub>v</sub> at 25°C**

<b>Carbon monoxide</b>	<b>1145</b>
<b>Nitric oxide</b>	<b>1230</b>
<b>Nitrogen dioxide</b>	<b>1850</b>
<b>Ozone</b>	<b>1963</b>
<b>Sulfur dioxide</b>	<b>2617</b>

**Table 3 Examples of Emission limits**

	<b>CO (g/km)</b>	<b>HC + NO<sub>x</sub> (g/km)</b>
<b>BS I</b>	<b>2.72/3.16</b>	<b>0.97/1.30</b>
<b>BS II</b>	<b>2.20</b>	<b>0.50</b>
		<b>HC      NO<sub>x</sub></b>

BS III	2.30	0.20	0.15
BS IV	1.00	0.10	0.08

### **Methods of gas concentration measurement:**

Broadly the gas concentration methods may be classified as Non separation methods and Separation methods. In the former there is no effort made to isolate the candidate gas from the gas mixture. In the latter the candidate gas is physically separated before being measured. We shall describe a few of the methods available in these two broad categories.

#### **(i) Non separation methods:**

- (a) Non Dispersive Infrared Analyzed (NDIR)
- (b) Differential Absorption LIDAR (DIAL)
- (c) Chemiluminescence NO<sub>x</sub> detection

#### **(ii) Separation methods:**

- (a) Gas Chromatography
- (b) Orsat gas analyzer

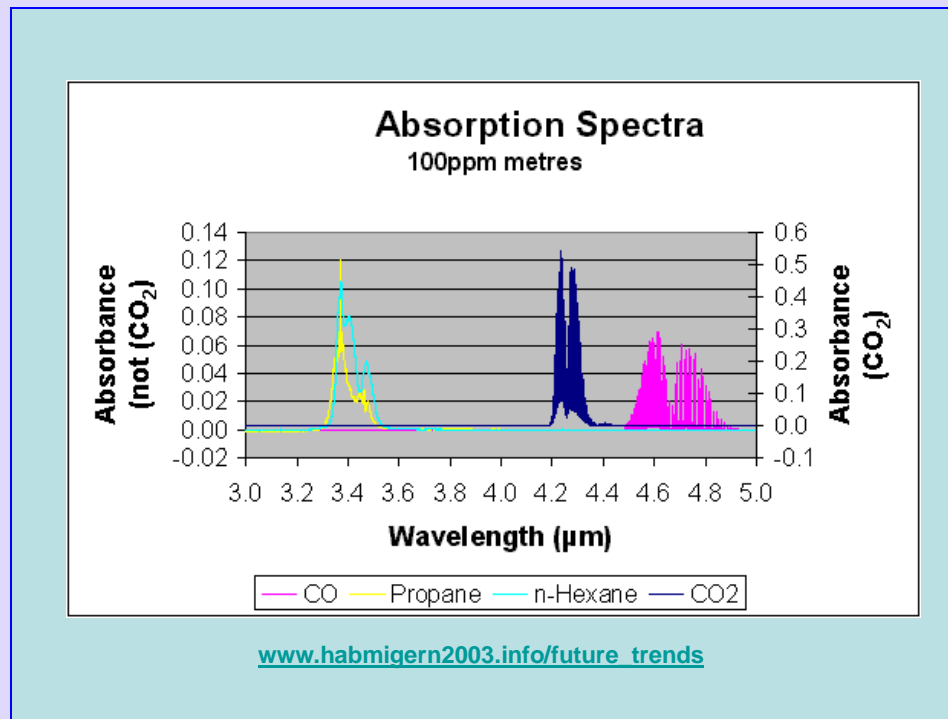
These are discussed in detail in what follows.

#### **(i) Non separation methods**

##### **(a) Non Dispersive Infrared Analyzed (NDIR)**

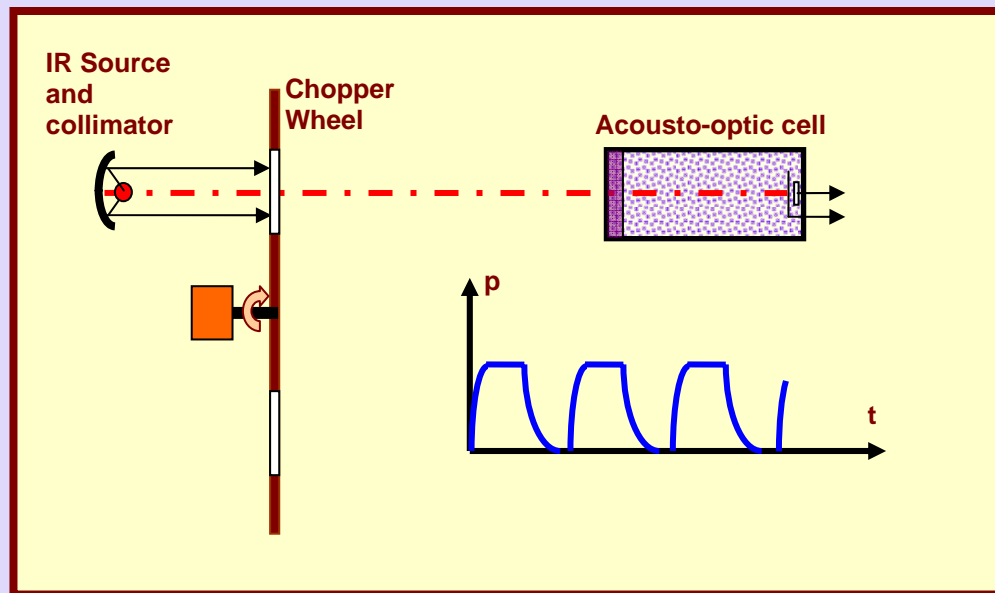
Most of the pollutant gases that are of interest to us absorb in the infrared part of the electromagnetic spectrum. The absorption by a gas depends on the concentration level and also the path length over which the electromagnetic radiation travels through the gas. For example absorption spectra of common

gaseous pollutants are shown in Figure 34 for concentration path length product of 100 ppm m.



**Figure 34 Absorption bands of common gases**

It is seen that small concentrations of the pollutant gases are measurable based on absorption of radiation of suitable wavelength even when the gas sample contains a mixture of these gases. In principle there is thus no need to separate the candidate gas from the mixture before making the measurement of concentration. One of the most popular methods is the non dispersive infrared detection where the radiation used is broad band radiation. No monochromator (refer our discussion of radiation properties earlier) is required in this method. Just how a particular gas is detected will become clear from the discussion on the acousto-optic detector that follows.



**Figure 35 Schematic of an acousto-optic cell**

Figure 35 shows the constructional details of an acousto-optic cell. The cell consists of a rigid vessel that contains the gas that is to be detected. Collimated infrared radiation is allowed in to the cell through a suitable window. The infrared radiation is chopped using a wheel with a set of holes arranged along the periphery of the wheel. The wheel is rotated at a constant speed using a suitable motor. A pressure transducer (usually a condenser microphone, see discussion on pressure measurement) is placed within the acousto-optic cell as shown. When the infrared radiation passes into the cell a part of it which is in the absorption band of the gas is absorbed by the candidate gas. This heats the gas and since the gas is confined within a rigid vessel, the volume is held fixed and hence the pressure goes up. When the incoming radiation is chopped (it enters the cell intermittently) the pressure within the cell varies as shown schematically in Figure 35. The pressure transducer picks up this and generates a signal proportional to the pressure change. The pressure change is a function of the candidate gas concentration within the cell. Any way the cell is initially filled with

a certain concentration of the candidate gas and sealed so that the pressure change is proportional to the amount of infrared radiation that enters it.

Now consider the situation shown in Figure 36 where a sample cell is placed in the path of infrared radiation in front of the acousto-optic cell. The sample cell is provided with two windows that allow the infrared radiation to pass through with negligible absorption. If the sample cell contains a certain concentration of the candidate gas that is also contained in the acousto-optic cell the amount of radiation in the absorption band of the candidate passed on in to the acousto-optic cell is less than when the sample cell is absent or the sample gas does not contain the candidate gas. It is thus clear that the pressure change in the acousto-optic cell is reduced in direct proportion to the concentration of the candidate gas in the sample cell.

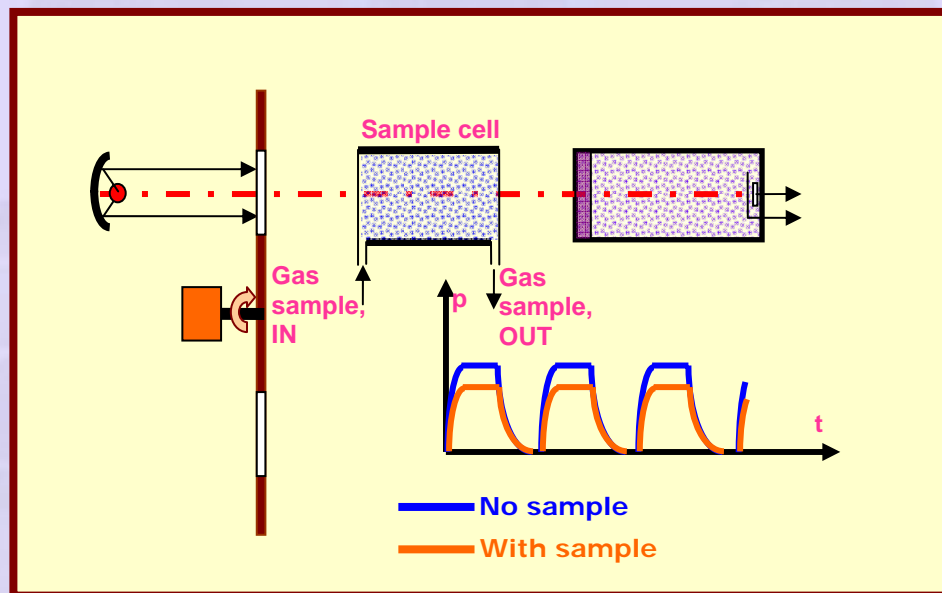
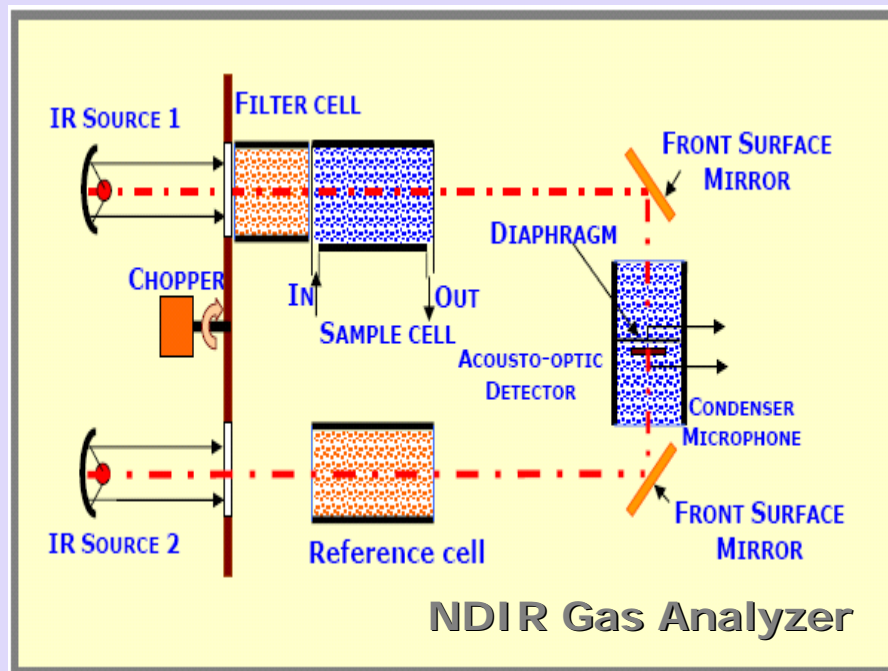


Figure 36 Sketch for explaining the principle of NDIR





**Figure 37 Details of NDIR system**

We are now ready to describe a full fledged NDIR system. Figure 37 shows all the components of NDIR. The instrument is a double beam instrument with two IR sources with collimating optics. The beam 2 is a reference beam that sends the infrared radiation through a reference cell that contains all other gases (including gases that have absorption overlap with the candidate gas) in the sample other than the candidate gas. There is thus no absorption of the band that is absorbed by the candidate gas. Beam 1 passes through the sample gas cell as well as a filter cell that contains large concentration of those gases that have significant absorption in a region that overlaps absorption by the candidate gas. This way only the radiation that is absorbed by the candidate gas is available for absorption by the sample cell. The acousto-optic detector is now in the form of a two chambered device with a diaphragm between the two chambers. Beam 1 and beam 2 are sent in to the two chambers that are formed by the diaphragm. The diaphragm also forms a part of a condenser microphone as shown in the figure. The microphone thus responds to the difference in

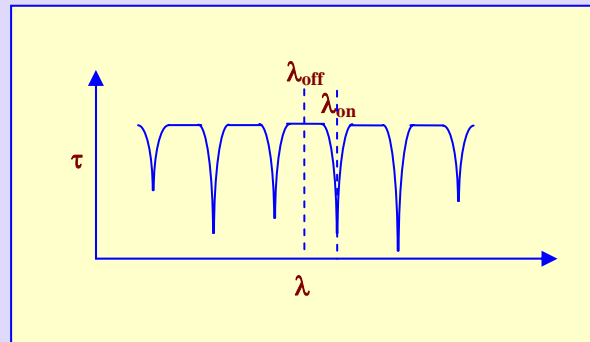
pressure across it. The signal thus developed is proportional to the concentration of the candidate gas in the sample cell. Calibration of the instrument is possible with special gas mixture having known concentrations of candidate gas in the mixture taken in the sample cell. The NDIR needs to use different filter cells and acousto-optic detectors for different gases.

For example NDIR is used for monitoring CO in ambient air. The concentration may be between 0 and 100 ppm<sub>v</sub>. The IR radiation used is in the 4 – 4.5 μm range. CO in flue gases may vary between 0 – 250 ppm<sub>v</sub> to as high as 1% by volume. NDIR is also useful for measuring SO<sub>2</sub> and NO<sub>x</sub> in flue gases. In the case of NO<sub>x</sub> removal of interference by CO<sub>2</sub>, SO<sub>2</sub>, water and Hydrocarbons is necessary while in the measurement of SO<sub>2</sub> interference by NO<sub>2</sub> is to be removed.

### **(b) Differential Absorption LIDAR (DIAL)**

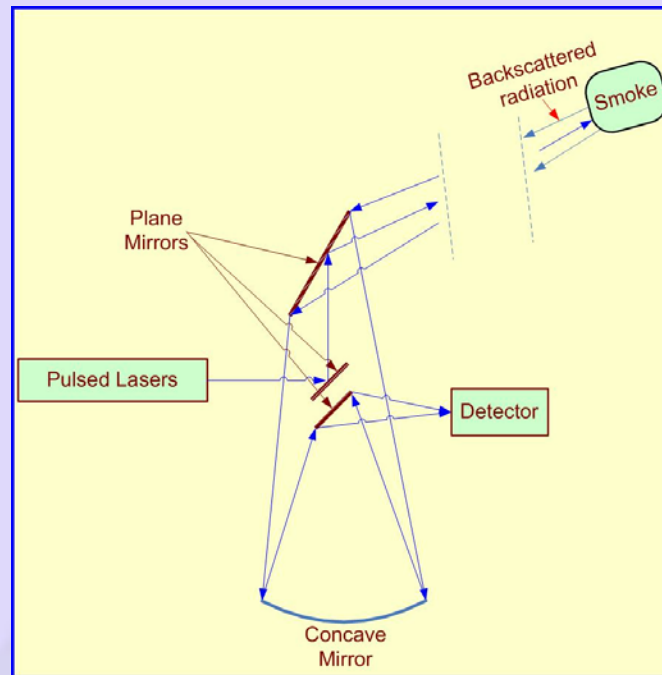
Remote measurement of gas concentration in the atmosphere is necessitated because of difficulties in measurement in situ and also because of large path lengths involved. Either airborne or satellite based or ground based instruments are required to make gas concentration measurements. For example, airborne measurement of atmospheric water vapor is possible using differential absorption. Differential absorption uses two wavelengths of laser radiation that are close to each other such that they behave similarly as they pass through the atmosphere except for the fact that radiation at one of the wavelengths is strongly absorbed by the candidate gas while radiation at the second wavelength suffers negligible absorption by the candidate gas. Most gases present in the

atmosphere exhibit band structure with fine structure i.e. have several discrete wavelengths or lines within the band over which absorption takes place.



**Figure 38 Principle of differential absorption**

Figure 38 shows the choice of the two wavelengths for differential absorption. The ordinate shows the transmittance  $\tau$ . Smaller the  $\tau$  larger is the absorption. The wavelength corresponding to that close to the center of the 'line' is referred to as  $\lambda_{on}$  while that in the space between two 'lines' is referred to as  $\lambda_{off}$ . Radiation at  $\lambda_{on}$  suffers significant absorption while radiation at  $\lambda_{off}$  suffers very little absorption. However all other phenomena like scattering by particulate matter and reflection from clouds etc. are virtually the same for the two wavelengths since they are chosen very close to each other. For example, in a specific case the two wavelengths are chosen between  $0.813 - 0.818 \mu\text{m}$ .



**Figure 39 Schematic of a Differential Absorption Laser system**

Schematic of the DIAL system is shown in Figure 39. It consists of pulsed lasers working at two wavelengths needed for differential absorption, optical arrangement for sending these two laser beams through the atmosphere, collection optics to collect the backscattered radiation and then detectors to take a ratio of the two signals to get the concentration of the candidate gas. Backscatter may take place from smoke or cloud or a target placed on a balloon or some such arrangement. Apart from absorption the beams will undergo attenuation of the intensity due to beam divergence, scattering by particulates and transmission losses in the optics. As mentioned earlier all these are the same for both wavelengths. The path lengths for both the laser beams are also the same.

For the beam at wavelength  $\lambda_{on}$  the cross section is the sum of absorption cross section  $\sigma_{abs}$  and all other processes represented by  $\sigma_{sca}$ . Thus the total

absorption cross section is  $\sigma_{tot} = \sigma_{abs} + \sigma_{sca}$ . For the beam at wavelength  $\lambda_{off}$  the cross section is just  $\sigma_{sca}$ .

By Beer's law we know that the attenuation of radiation follows the relation  $I_{\lambda} = I_{\lambda,0} e^{-c\sigma L}$  where  $I_{\lambda}$  the intensity of radiation transmitted across a path length of  $L$ ,  $I_{\lambda,0}$  is the intensity of entering radiation,  $c$  is the concentration of the candidate gas and  $\sigma$  is the total cross section. We apply Beer's law to the laser radiation at the two wavelengths to get

$$I_{\lambda_{on}} = I_{\lambda_{on},0} e^{-c(\sigma_{abs} + \sigma_{sca})L}; I_{\lambda_{off}} = I_{\lambda_{off},0} e^{-c\sigma_{sca}L} \quad (37)$$

It will of course good to choose the intensities at the two wavelengths the same

even though it is not really necessary. The ratios  $R_1 = \frac{I_{\lambda_{on}}}{I_{\lambda_{on},0}}$ ,  $R_2 = \frac{I_{\lambda_{off}}}{I_{\lambda_{off},0}}$  are

estimated from the measured intensity values. Using Expressions 37 we see that

$$\frac{R_1}{R_2} = \frac{e^{-c(\sigma_{abs} + \sigma_{sca})L}}{e^{-c\sigma_{sca}L}} = e^{-c\sigma_{abs}L} \quad (38)$$

If the absorption cross section is known the concentration of the candidate gas is given by

$$c = -\frac{1}{\sigma_{abs}L} \ln\left(\frac{R_1}{R_2}\right) \quad (39)$$

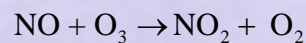
In practice the laser source is pulsed with a known pulse width as well repetition rate. The return signal may be gated such that the signal is collected after a known time delay thus making it possible to vary or choose the required path length (this is similar to the pulse echo method using ultrasound discussed earlier). The ratios in Equation 38 are averaged over a large number of shots of

the lasers and averaged to improve signal to noise ratio. The detector used is a high sensitivity Avalanche Photo Diode (APD).

An example of this is the “LIDAR Atmospheric Sensing Experiment or LASE of NASA” for airborne water vapor measurement. This is capable of measuring water concentration in the range of 0.01 g/kg to 20 g/kg (this is also referred to as the specific humidity). Aerosol backscatter ratios can be measured from ground to 20 km with a vertical resolution of 30 m and a horizontal resolution of 40 m. The system uses an aircraft borne LIDAR to make water concentration measurements. Table 4 gives the specifications for the system.

### **(c) Chemiluminescence NO<sub>x</sub> detection**

As mentioned earlier NO<sub>x</sub> refers to a combination of both NO and NO<sub>2</sub>. If NO<sub>x</sub> is subject to high temperature of around 1000°C NO<sub>2</sub> breaks down to NO. The sample will thus contain only NO. If NO is reacted with ozone the following exothermic reaction takes place.



Since the reaction is exothermic the NO<sub>2</sub> formed is in the excited state and hence emits radiation. This is called Chemiluminescence. The emitted radiation is proportional to the concentration of NO<sub>2</sub> and hence provides a method of measuring NO<sub>x</sub> concentration. Schematic of the chemiluminescent NO<sub>x</sub> analyzer is shown in Figure 40.

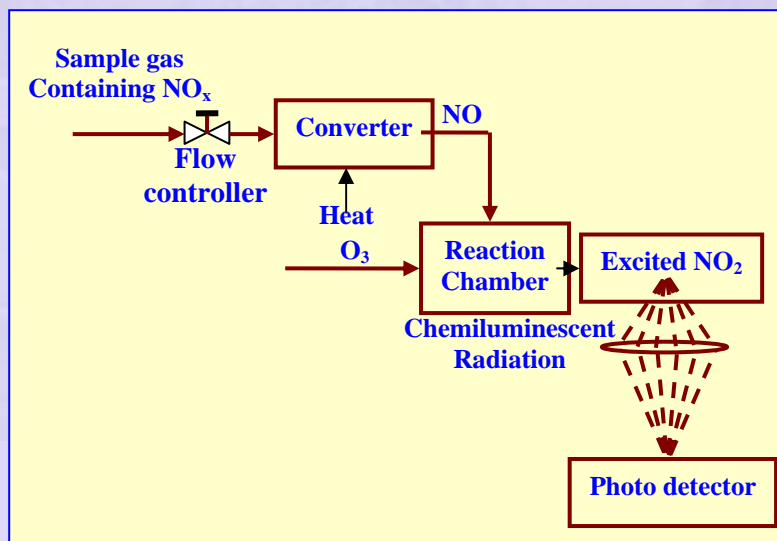
**Table 4 LASE H<sub>2</sub>O DIAL Parameters**  
a) Transmitter

<b>Energy</b>	<b>150 mJ (On and Off)</b>
<b>Line Width</b>	<b>0.25 pm</b>
<b>Repetition Rate</b>	<b>5 Hz</b>
<b>Wavelength</b>	<b>813 – 818 nm</b>
<b>Beam divergence</b>	<b>0.6 mrad</b>
<b>Pulse Width</b>	<b>50 ns</b>
<b>Aircraft Altitude</b>	<b>16 – 21 km</b>
<b>Aircraft Velocity</b>	<b>200 m/s (720 km/h)</b>

b) Receiver

<b>Effective Area</b>	<b>0.11 m<sup>2</sup></b>
<b>Field of View</b>	<b>1.1 mrad</b>
<b>Filter Bandwidth (FWHM)</b>	<b>0.4 nm (Day), 1 nm (Night)</b>
<b>Optical Transmittance (Total)</b>	<b>23% (Day), 49% (Night)</b>
<b>Detector Efficiency</b>	<b>80% Silicon APD</b>
<b>Noise Equivalent Power</b>	<b>2.5×10<sup>-14</sup> W/Hz<sup>1/2</sup> (At 1.6 MHz)</b>
<b>Excess Noise Factor (APD)</b>	<b>2.5</b>

Refer to the web site: [asd-www.larc.nasa.gov/lase](http://asd-www.larc.nasa.gov/lase)



**Figure 40 Chemiluminescent NO<sub>x</sub> analyzer**

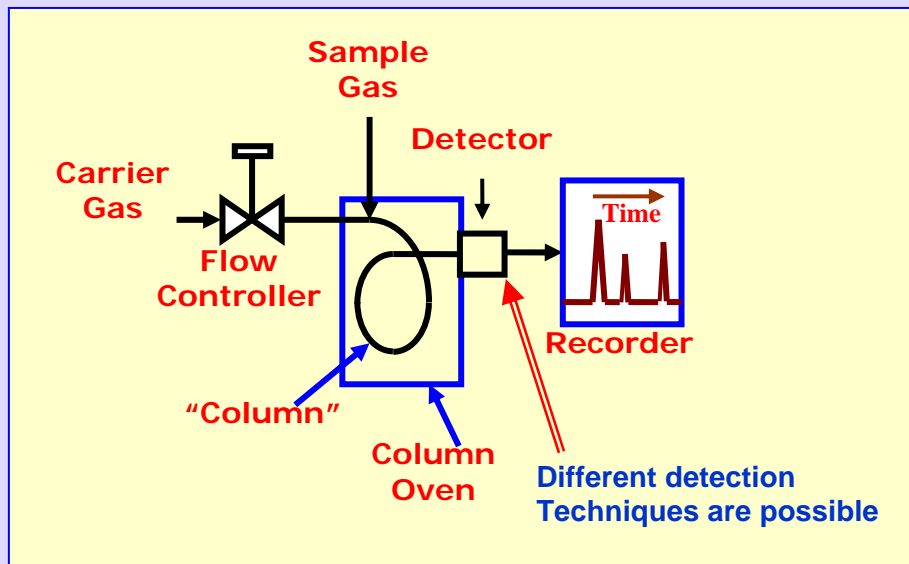
The required flow rate of the sample gas is maintained by adjusting the flow controller. The sample gas is heated to convert  $\text{NO}_x$  to NO. In the reactor, NO reacts with  $\text{O}_3$  to generate  $\text{NO}_2$  in the excited state. The emitted radiation from the stream of excited  $\text{NO}_2$  is collected by suitable optics and measured by the photo detector. The signal is related to the concentration of  $\text{NO}_x$  in the sample.

## **(ii) Separation methods**

### **(a) Gas Chromatography**

Gas chromatography is a technique by which a pulse of gas mixture is physically separated into its constituents that arrive at a suitable detector as temporally separated pulses. The separation takes place in a gas chromatograph column or GC column that contains a suitable adsorbent. As the gas mixture which is carried along with a carrier gas (like Helium) moves through the column different constituents in the gas mixture pass through at different speeds (they are adsorbed and eluted or released at different rates) and hence get separated as the mixture covers a long path through the column. The first to arrive out of the column is the carrier gas. Other gases arrive as temporally separated pulses. The concentration of each gas is ascertained from these pulses.





**Figure 41 Schematic of a gas chromatograph**

Schematic of a gas chromatograph is shown in Figure 41. A controlled carrier gas flow is maintained using the flow controller. A small metered amount of sample gas is added to it at a point downstream of the flow controller and before the gas chromatograph column. The column is in the form of coil of a capillary whose inside surface is coated with a suitable adsorber. A suitable detector at the end of the column completes the chromatograph instrument. The column is maintained at a constant temperature by placing the column inside an oven as shown. As shown in the figure it is possible to use different techniques to measure the concentration of the constituent gases in the mixture.

Some of the detection techniques are:

- Thermal conductivity detector
- Infrared spectrometer – The method is referred to as GC IR
- Mass spectrometer – The method is referred to as GC MS
- Flame ionization detector (or FID)

### Thermal conductivity detector

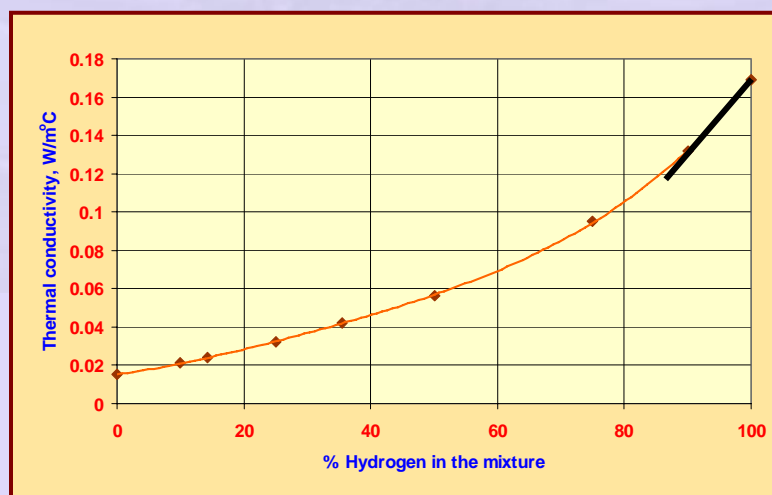
Thermal conductivity detector is akin to the Pirani gauge that was discussed in the measurement of vacuum. At the exit of the GC column a steady stream of carrier gas will emerge with carrier gas and a candidate gas in the sample gas at some interval after the sample gas is injected in to the carrier gas stream. The thermal conductivity of the candidate gas is, in general, different from that of the carrier gas. Examples of thermal conductivities of different gases of interest to us are given in Table 5. The thermal conductivity values are normalized with respect to thermal conductivity of dry air. Either argon or helium may be used as carrier gas. Gases whose relative thermal conductivities are close to one another are not resolved well. However, with prior knowledge it is possible to resolve these.

**Table 5 Relative thermal conductivities of various gases**

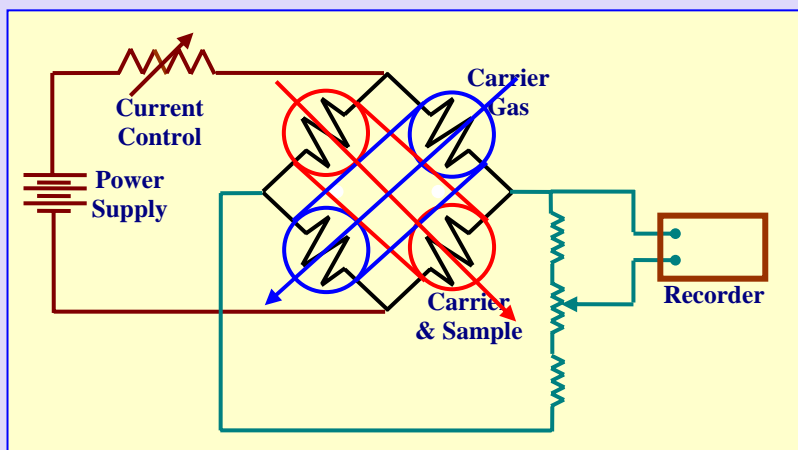
Gas	Relative thermal conductivity
Air	1.00
Argon	0.63 (Carrier gas)
Carbon dioxide	0.55
Carbon monoxide	0.88
Chlorine	0.30
Ethane	0.69
Ethylene	0.65
Helium	5.42 (Carrier gas)
Hydrogen	6.39
Nitric oxide	0.90
Nitrogen	0.92
Nitrous oxide	0.57
Oxygen	0.92
Sulfur dioxide	0.31
Water vapor	0.63

Thermal conductivity of a mixture of Hydrogen and carbon dioxide varies with percentage of Hydrogen in the mixture as shown in Figure 42. We see that if Hydrogen is present in small quantities the thermal conductivity varies more or less linearly with  $H_2$  concentration as indicated by the black line. Up to about 10%  $H_2$  the linear relation appears to hold.

Thermal conductivity detector is shown schematically in Figure 43. It essentially consists of full bridge circuit with four cells containing heated wires. Two of these are bathed by a stream of carrier gas while the other two are bathed by carrier gas plus the candidate gas whenever it emerges out of the GC column. When all the heated wires are bathed by carrier gas alone, the bridge is under balance. Whenever the candidate gas is also present the thermal conductivity changes and the bridge goes out of balance. This is because of the slight change in the temperature of the wire in contact with the candidate gas. The imbalance potential difference  $V$  is recorded and the output of the instrument looks schematically like that shown in Figure 41. Calibration of the instrument is possible using sample mixtures of known composition. Limit of detection is around  $0.4 \text{ mg/m}^3$ .



**Figure 42 Thermal conductivity of a mixture of Hydrogen and Carbon dioxide**



**Figure 43 Thermal conductivity detector schematic**

### **GC with Infrared spectrometer – GC IR**

The GC column is interfaced with an infrared spectrometer as detector for measuring the gas concentration. The stream coming out of the GC column is sent through a cell which is placed in the path of the IR beam in an IR spectrophotometer. The absorption in a suitable absorption band of the candidate gas may be used to determine the candidate gas composition using Beer's law.

### **GC with Mass spectrometer –GC MS**

The GC column is interfaced with a mass spectrometer as detector for measuring the gas concentration. A mass spectrum of the gas stream emerging from the GC column is recorded. The peak heights of different mass fragments may be calibrated with gas mixtures of known composition.

### Flame ionization detector (or FID)

Total hydrocarbon analyzer or THC estimates the total hydrocarbon by the use of a flame ionization detector or FID. If a gas chromatograph is used it is possible to determine the concentrations of different hydrocarbons present in the gas sample. When a hydrocarbon is burnt in a hydrogen flame HC is broken down into ions. The ion current is measured and related to the HC concentration.

### (b) Orsat gas analyzer

Flue gas composition in power plants helps us in determining how well the combustion system is functioning. Even though on line monitoring systems are common in modern power plants it is instructive to look at the use of an Orsat gas analyzer. Orsat Analyzer determines the volume fraction of individual gases in a mixture by selective absorption of the constituents by a reagent and the consequent reduction in volume of a sample gas mixture. Reagents that are used are:

- For absorption of  $\text{CO}_2$  it is 40% solution of potassium hydroxide
- Mixture of Pyrogalllic acid (1,2,3 – Trihydroxybenzene) and solution of KOH is used for absorption of oxygen
- Alternately it is Chromos chloride (Chromium dichloride) for absorption of oxygen
- Alternately Copper mono chloride ( $\text{CuCl}$ ) may be used as the reagent for absorption of CO

Analysis is by absorption and determination is made in the following order:  $\text{CO}_2$  first, Oxygen next and CO last.

The measurement is done manually by using an apparatus whose appearance is as indicated in the photograph given in Figure 44, taken from [www.psawcatalogue.com](http://www.psawcatalogue.com). A schematic diagram of the analyzer is shown as Figure 45, taken from - Agriculture Notes, John Faragher, "Measuring CA storage atmospheres with the Orsat Analyzer", AG 0281, ISSN 1392-8062, June 2000.

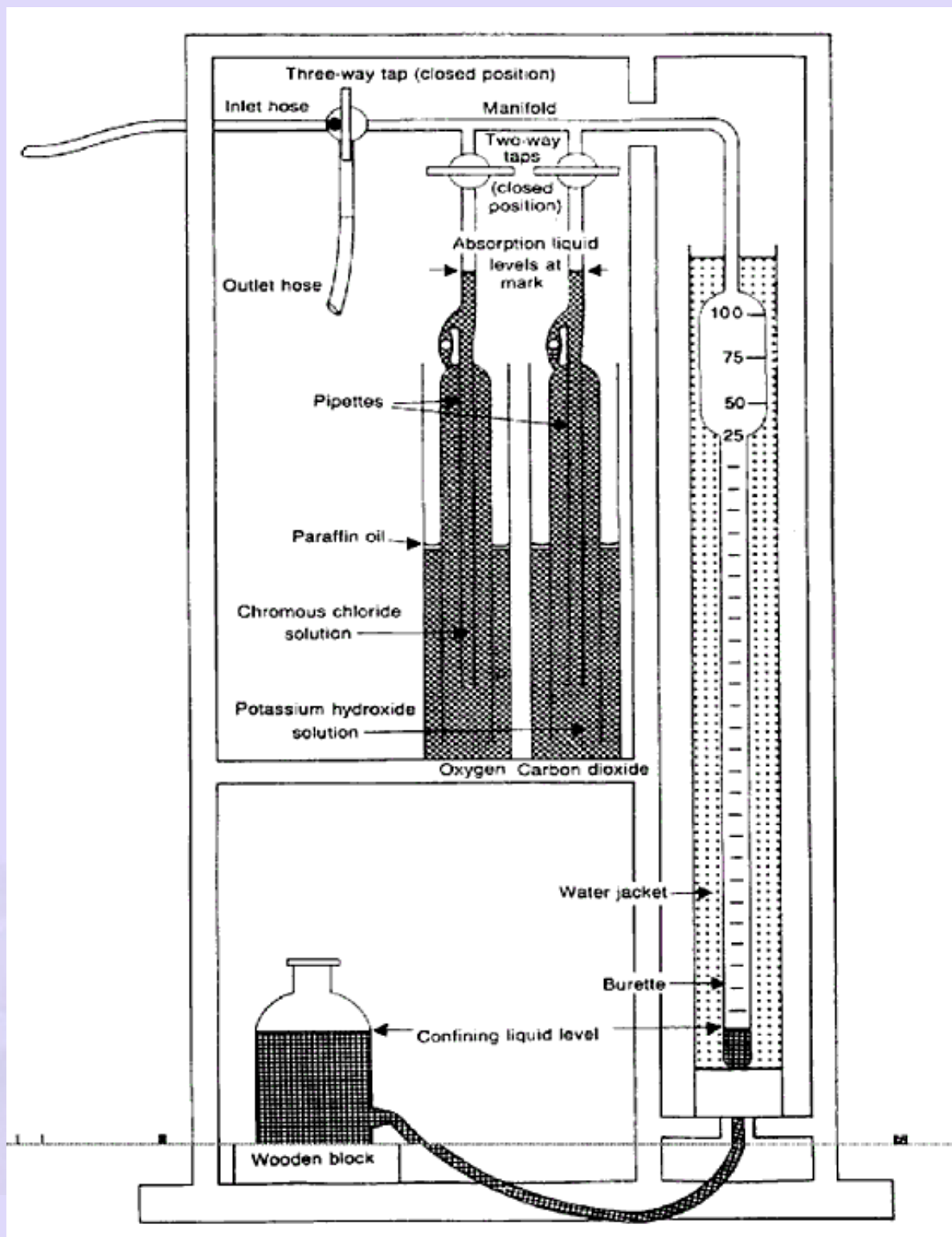


**Figure 44 Photograph of an Orsat analyzer**

Initially the apparatus is flushed with the sample gas by using the three way tap to trap samples repeatedly and flushing them out by rejecting them to the atmosphere by the use of the bottle containing the confining liquid. If it is raised so that the level of the confining fluid rises in the burette with both the two way taps in the closed position the gas within the apparatus may be released to atmosphere. If now the three way valve is opened to the inlet hose the gas sample may be allowed to enter the burette by lowering the bottle. As the level

of the liquid goes down the sample gas will fill the burette. This operation is repeated such that any gas that was present in the burette to start with is completely flushed by the sample gas. Once the sample gas has been taken in the three way tap is closed. The sample gas trapped in the burette may now be sent in to the absorbing liquid by opening the appropriate two way tap and rising the bottle. The sample gas comes in contact with the reagent and sufficient time is allowed for the absorption of the appropriate constituent gas to take place. The bottle is now lowered and the level of the liquid in the burette will indicate the change in the volume of the sample gas and hence the volume of the gas constituent that is absorbed by the reagent. The two way tap is closed and the operation repeated with the second reagent, third reagent and so on. For low  $\text{CO}_2$  (< 4% by volume) or high  $\text{O}_2$  (> 1.5%) the burette have 0.1 subdivisions.





**Figure 45 Schematic of an Orsat analyzer**



## Particulate matter – Soot (or smoke):

Most engines and furnaces used in power plants put out particulate matter in the form of soot or smoke. Soot/smoke refers to particles of unburnt carbon remaining after combustion of a hydrocarbon fuel. These particulates have very small size and cause pollution of the atmosphere. For example, the mean diameter of smoke particles in a diesel engine exhaust is about 30 nm. These may be measured either by collection and weighing or by measuring *opacity*

There are several issues that are to be considered in the measurement of smoke. These are basically related to sampling.

- ❖ Particle losses in sampling tube
  - Inertial losses
    - Especially in curved tubes due to centrifugal force field
  - Gravitational losses
    - In horizontal sampling tube due to settling of the particles under the action of gravity

These losses may be avoided by vertical orientation of the sampling tube

- ❖ Iso-kinetic sampling (collection and weighing method)

Iso-kinetic sampling is taking out or collecting a sample under dynamic conditions that prevail in the process. Velocity, temperature and pressure should not change during the collection process. If any of these changes the measurement may yield values that are not representative of the process. We look at the requirement that needs to be satisfied for iso-kinetic sampling to hold. For this purpose we define a parameter called

the Stokes number as  $Stk = \frac{\rho_p D_p^2 V_0}{18\mu L_{ch}}$  where  $D_p$  = Particle diameter,  $\rho_p$  = particle density,  $V_0$  = sample air velocity in the free stream,  $L_{ch}$  = characteristic dimension of the probe (possibly its diameter  $D_s$ ) and  $\mu$  is the kinematic viscosity of the fluid. Alternately it may also be defined by the relation  $Stk = \frac{\tau V_0}{D_s}$  where  $\tau$  = Particle relaxation time. The particle relaxation time may thus be identified as  $\tau = \frac{\rho_p D_p^2}{18\mu}$ . If  $Stk < 0.01$  sampling

is iso-kinetic.

- Sample probe should be aligned parallel to the gas stream
- Gas velocity entering the probe should be the same as the free gas stream velocity

Particles in a gas move with the same velocity as the gas if the diameter of the particle is small. Larger particles tend to move, for example, in a straight line when the gas encounters a change in direction. If the sampling is not iso-kinetic the velocity of the sample within the probe is different from the free stream velocity. There is a change in the velocity and the streamlines bend suitably to adjust to the flow field within the probe. It is thus possible that the larger or the smaller particles may not be sampled properly. Thus the measurement of particulates will under sample or over sample particles of different diameter particles in the sample.

Collection or capture efficiency of a sampling tube is dependent on the diameter and velocity. For non iso-kinetic conditions the collection efficiency is described by the formula

$$A(V, Stk) = 1 + \left( \frac{V_0}{V} - 1 \right) \left[ 1 - \frac{1}{1 + Stk \left( 2 + 0.63 \frac{V}{V_0} \right)} \right] \quad (40)$$

In Equation 40  $V$  is the flow velocity in the sampling tube. The collection efficiency is defined as the ratio of the concentration in the sampled flow to that in the free stream, for particles of a specified diameter.

### Example 12

*Determine the diameter of a sampling tube if the largest particle diameter is expected to be  $2 \mu\text{m}$ . Particle density is specified to be  $2500 \text{ kg/m}^3$ .*

*Other pertinent data:  $V_0 = 2 \text{ m/s}$  and flow rate through sample tube is not to be less than  $100 \text{ ml/s}$ . The sample gas is air at 1 atmosphere pressure and  $25^\circ\text{C}$ .*

*We shall design the sample tube for a flow rate of*

$$Q = 100 \text{ ml/s} = 100 \times 10^{-6} = 10^{-4} \text{ m}^3 / \text{s}$$

*The diameter of the sampling tube is then determined as*

$$D_s = \sqrt{\frac{4Q}{\pi V_0}} = \sqrt{\frac{4 \times 10^{-4}}{\pi \times 2}} = 0.007979 \text{ m} \approx 0.008 \text{ m}$$

*We now calculate the Stokes number to determine whether the above diameter is satisfactory. We assume that the air sample is at 1 standard atmosphere and at a temperature of  $25^\circ\text{C}$ . Kinematic viscosity of air is  $\nu = 15.6 \times 10^{-6} \text{ m}^2 / \text{s}$ .*

*Diameter of largest particles is given to be  $D_p = 2 \mu\text{m} = 2 \times 10^{-6} \text{ m}$ . The Stokes number is then given by*

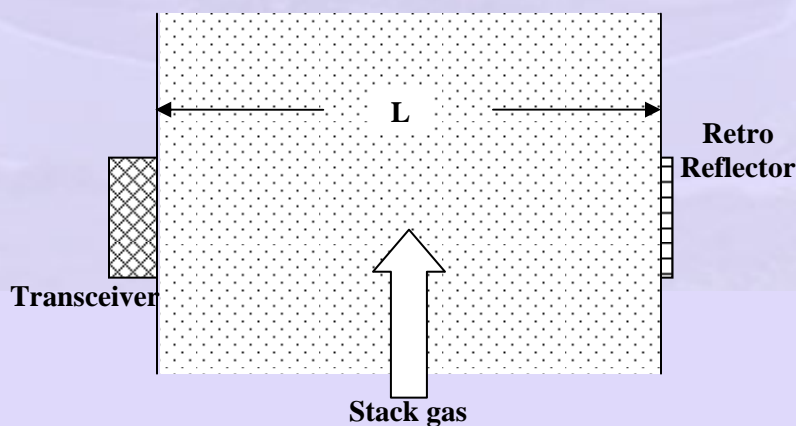
$$Stk = \frac{D_p^2 \rho_p V_0}{18 \mu D_s} = \frac{(2 \times 10^{-6})^2 \times 2500 \times 2}{18 \times 18.5 \times 10^{-6} \times 0.008} = 0.00752 \approx 0.008$$

*Since this is less than 0.01, the sampling tube of 0.008 m diameter is satisfactory.*

Collection of particulate matter may be accomplished by drawing or aspirating the particulate laden gas through a filter paper or a membrane. Filter paper is useful for particles between 0.5 and 1  $\mu\text{m}$  while a membrane may be useful down to 0.1 $\mu\text{m}$ . The filter is operated for a measured duration during which the particles collect on the filter element. If the flow rate of the sample gas is maintained constant during the collection process we can calculate the volume of gas that has passed the filter element. The particulates collected may be determined either by weighing the filter element before and after the collection process or by measuring the optical transmittance of the filter element.

The measurement of opacity of flue gases may be made in situ in the stack without separating the particulates. Since no sample collection is involved many of the problems associated with sampling are obviated. Codes specify the way such a measurement is to be made. Telonic Berkeley TBM300 portable opacity meter is a suitable measuring device for this purpose.

#### Opacity meter:



**Figure 46 In situ opacity measurements in a stack**

Schematic of how an opacity meter may be used for in situ measurement of smoke in a stack is shown in Figure 46. The instrument is single ended and uses a light source detector combination as the transceiver. At the other end we have a retro reflector to return the light. The light source is normally a green LED (light emitting diode) with a spectral peak between 550 and 570 nm (0.55 and 0.57  $\mu\text{m}$ ). The receiver is a photo detector. An instrument available from Preferred Utilities Manufacturing Corporation (preferred Instruments Combustion Control) has the following specifications.

**Table 6 Specifications of an opacity meter**

<b>Spectral peak and mean width</b>	<b>500 – 600 nm</b>
<b>Angle of projection</b>	<b>&lt;5°</b>
<b>Response time</b>	<b>&lt;10 s for 95% change in opacity</b>
<b>Sighting distance</b>	<b>1 to 8 ft (0.3 to 2.5 m) smoke duct 3 to 10 ft (1 to 3 m) path length</b>
<b>Accuracy</b>	<b>±1%</b>
<b>Calibration drift</b>	<b>&lt;0.5 %</b>

Instrument is double ended with light source and detector facing each other. Opacity is defined as 1 minus the transmittance, a quantity that was introduced earlier during the discussion on differential absorption technique. We define an extinction coefficient  $\beta$  to account for loss of intensity due to absorption and scattering by the particulates present in the stack gas. This factor may be related to the particle density if we know the extinction cross section of the particles. Example 13 demonstrates this.

### Example 13

Smoke opacity has been measured by a double ended system to be 40%. The path length has been noted to be 10 cm. The temperature of the gas is 30°C. It has been ascertained that the soot density is  $\rho_s = 600 \mu\text{g}/\text{m}^3$ . What is the extinction cross section of soot particles? If the soot may be considered as carbon particles with a mean diameter of  $D_p = 0.2 \mu\text{m}$ , and of density  $\rho_c = 2300 \text{ kg}/\text{m}^3$  determine the number density of soot particles.

Opacity of the gas is given to be 40%. Thus the transmittance of the gas is  $100 - 40 = 60\%$ . By definition we have  $\text{Transmittance} = Tr = e^{-\beta L} = 0.60$ . Noting that the path length is  $L = 0.1 \text{ m}$ , taking natural logarithms, we get

$$\beta = -\frac{1}{L} \ln(Tr) = -\frac{1}{0.1} \ln(0.6) = 5.1083 \text{ m}^{-1}$$

The extinction coefficient may also be written as the product of soot density and the extinction cross section. Thus

$$\beta = \sigma_e \rho_s \text{ or } \sigma_e = \frac{\beta}{\rho_s} = \frac{5.1083}{600 \times 10^{-6}} = 8513.8 \text{ m}^2 / \text{kg}$$

The mass of each particle may be obtained from the given data as

$$m_p = \rho_c \frac{\pi}{6} D_p^3 = 2300 \times \frac{\pi}{6} \times (0.2 \times 10^{-6})^3 = 9.6342 \times 10^{-18} \text{ kg}$$

We see that the soot density is the product of number density and the mass of each particle. Hence the number density  $N$  is determined as

$$N = \frac{\rho_s}{m_p} = \frac{600 \times 10^{-6}}{9.6342 \times 10^{-18}} = 6.228 \times 10^{13} \text{ particles} / \text{m}^3$$