Mechanical Measurements and Metrology
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Module - 4
Lecture - 43
Measurement of Gas composition (continued)

This will be lecture 43 on our on going series on Mechanical Measurements. Towards the end of the last lecture we were actually looking at measurement of concentration of gases using so called non separation methods.

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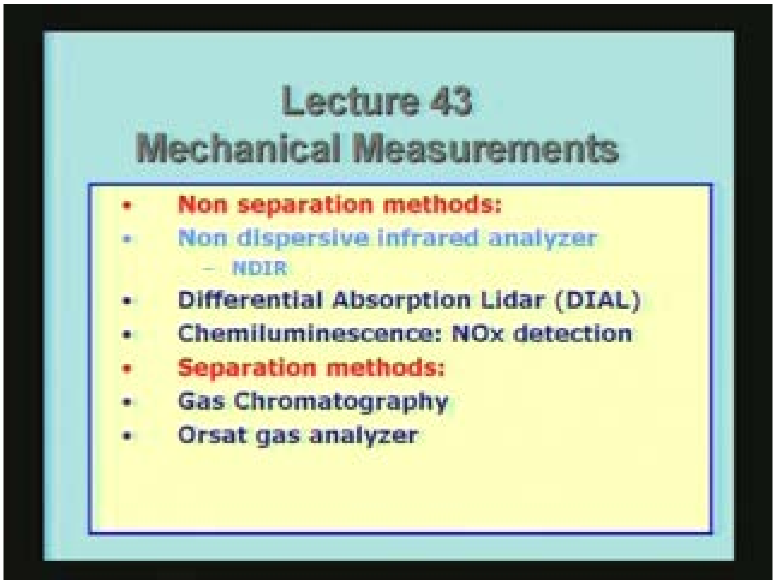
Lecture 43
Mechanical Measurements

- Non separation methods:
- Non dispersive infrared analyzer
  - NDIR
- Differential Absorption Lidar (DIAL)
- Chemiluminescence: NOx detection
- Separation methods:
- Gas Chromatography
- Orsat gas analyzer

In fact, in the previous lecture we have covered already the non dispersive infrared analyzer, which is a very useful instrument which is used in day-to-day laboratory practice for measuring especially exhaust gases from IC engines. The second one I was trying to describe in some detail was the differential absorption Lidar. Lidar stands for light detection and ranging and the particular technique is called dial or differential absorption Lidar.

I was explaining the principle of the Lidar for the differential absorption scheme. The basis is, of course, called the Beer's law, which assumes or which postulates there is an exponential decrease in the intensity of light which passes through an absorbing medium.

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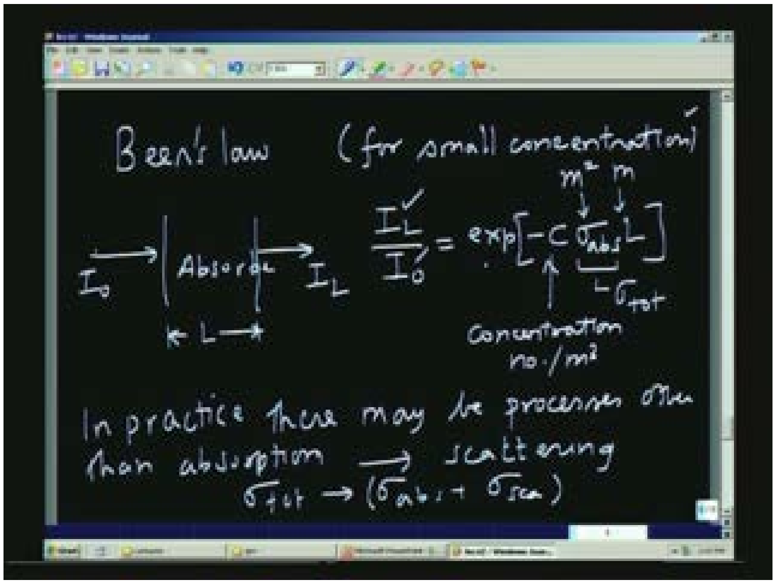

Beer's law (for small concentration)

$$\frac{I_L}{I_0} = \exp\Big[-\underset{\substack{\uparrow \\ \text{Concentration} \\ \text{no./m}^3}}{C}\ \underbrace{\overset{m^2}{\sigma_{abs}}}_{\sigma_{tot}}\ \overset{m}{L}\Big]$$

In practice there may be processes other than absorption $\longrightarrow$ scattering

$$\sigma_{tot} \rightarrow (\sigma_{abs} + \sigma_{sca})$$

In this case, we are looking at a particular wavelength at which some absorption is expected of a particular gas which exists in some concentration within that medium. There may be other gases present, which are not going to be influencing the absorption process. For example, if you remember, I talked about the lambda$_{on}$ and lambda$_{off}$. Lambda$_{on}$ is the wavelength or the frequency, at which the light will be absorbed by the particular gas which I am interested in. It may be water vapor for example, or carbon monoxide, carbon dioxide or any of the gases which we may be interested in.

And I have lambda$_{off}$ the frequency which is very close to lambda$_{on}$ but it is such that there is no absorption by the specie at that particular wavelength or the frequency. So, differential absorption means that, there is a difference in the absorption capability of the particular gas, because these two wavelengths have this particular property. One wavelength is absorbed, but the other one is not. Let us look at what is going to happen to the light which is passing through the medium. L is the thickness of the medium, or the extent of the medium, the incident radiation is I_0 at a particular wavelength which is of interest to us, and what is leaving this absorber is I_L.

I_L is the intensity as it leaves the layer of medium which may or may not absorb depending on the frequency of the radiation. So the Beer's law states that, I_L by I_0, the ratio of the emerging intensity to the incident intensity is e power minus c where, c is the concentration in numbers by m cube of the particular species, I am interested in, $\text{sigma}_{\text{absorption}}$ is the absorption cross section and L is the length of the passage through the medium. In fact, I, have to add something else to $\text{sigma}_{\text{absorption}}$. In practice, what will happen is, there may be other processes which will take place, processes other than absorption.

What are these processes which may take place?
One of them is, of course, scattering. In principle, what I have to do is this $\text{sigma}_{\text{absorption}}$, I have to augment by this scattering process so it is usually additive because, the concentration we are talking about is very small, it is usually additive. Therefore we can replace this by what we call as $\text{sigma}_{\text{total}}$, which will be sum of $\text{sigma}_{\text{absorption}}$ plus $\text{sigma}_{\text{scattering}}$. So, if you see here e to the power minus c into some summation of two quantities here can be written as this. So, I have I_L by I_0 is the ratio of the two intensities equal to exponential of minus c the concentration multiplied by sigma so I will add these two $\text{sigma}_{\text{absorption}}$ plus $\text{sigma}_{\text{scattering}}$ multiplied by L, and this can be written as e to the power minus c sigma multiplied by exponential of minus c $\text{sigma}_{\text{scattering}}$ intensity.

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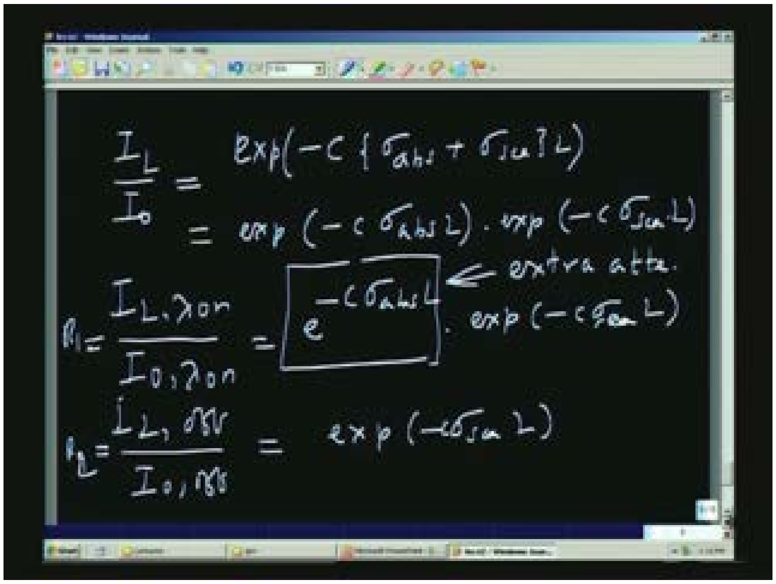

$$\frac{I_L}{I_0} = \exp(-c\{\sigma_{abs} + \sigma_{sca}\}L)$$
$$= \exp(-c\,\sigma_{abs}L)\cdot\exp(-c\,\sigma_{sca}L)$$
$$R_1 = \frac{I_{L,\lambda on}}{I_{0,\lambda on}} = \boxed{e^{-c\sigma_{abs}L}}\cdot\exp(-c\,\sigma_{sca}L) \Leftarrow \text{extra atte.}$$
$$R_2 = \frac{I_{L,off}}{I_{0,off}} = \exp(-c\,\sigma_{sca}L)$$

Suppose, I write similar equations for both the on and off frequencies we will see that I_L this will be $\text{lambda}_{\text{on}}$ divided by I_0 $\text{lambda}_{\text{on}}$ will be the same expression e to the power minus c $\text{sigma}_{\text{absorption}}$ L multiplied by this quantity, whereas $I_{L,off}$ divided by $I_{0,off}$ this will be absent and this will be simply given by e to the power minus c $\text{sigma}_{\text{scattering}}$ into L. This concentration is different from this concentration may be. For example, it could also include other concentrations of other species which may scatter. In fact I could have written c $\text{sigma}_{\text{absorption}}$ plus another c $\text{sigma}_{\text{scattering}}$.

The basic idea is that the attenuation, this ratio is called the attenuation is proportional to; this is the extra term, at the frequency of interest there is an extra attenuation. So this particular beam which travels the medium, and consists of frequency $\text{lambda}_{\text{on}}$ or wavelength $\text{lambda}_{\text{on}}$ suffers a certain extra attenuation. This is what we call as extra attenuation. So, if I take the ratio of these quantities in fact what I get is this quantity e to the power minus c $\text{sigma}_{\text{absorption}}$ multiplied by L and, if I know the quantity c absorption cross section, and if I know the length of travel within the medium, I can determine what the c is. c is actually logarithm of the other quantity, you can just take it. Let us call this is ratio one and we will say this is ratio 2, R_1 and R_2 so if you take the ratio of these two, the common factor will go off and you see that R_1 by R_2 will be actually e to the power minus c sigma and instead of giving that subscript I will just imagine it is already there so we will just simply write as c sigma L or if I take logarithms the minus c is equal to 1 by sigma L logarithm of R_1 by R_2.

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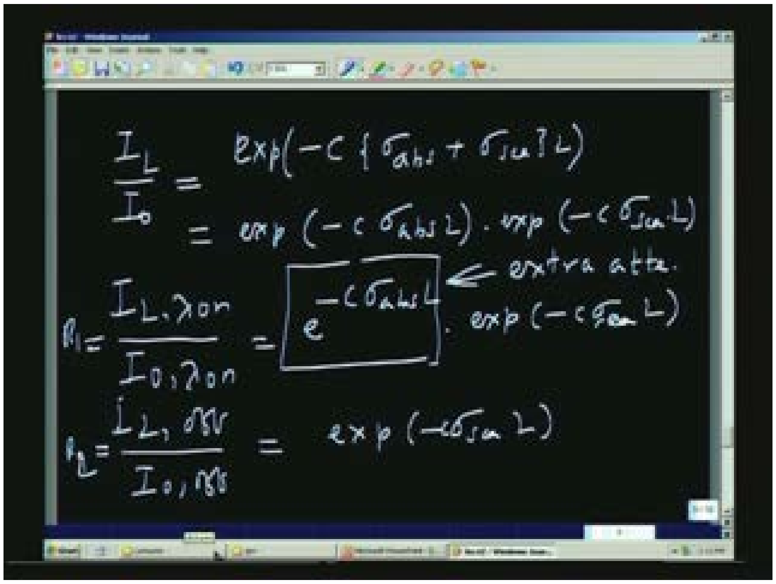

$$\frac{I_L}{I_0} = \exp(-c\{\sigma_{abs} + \sigma_{sca}\}L)$$

$$= \exp(-c\,\sigma_{abs}L)\cdot\exp(-c\,\sigma_{sca}L)$$

$$R_1 = \frac{I_{L,\lambda on}}{I_{0,\lambda on}} = \boxed{e^{-c\sigma_{abs}L}}\cdot\exp(-c\,\sigma_{sca}L) \Leftarrow \text{extra atte.}$$

$$R_2 = \frac{I_{L,\lambda off}}{I_{0,\lambda off}} = \exp(-c\,\sigma_{sca}L)$$

Since R_1 is smaller than R_2, this will be itself negative quantity, and therefore, minus c is equal to this that minus will cancel and this will give the concentration. So, basically the method of differential absorption consists of determining the ratio of the two quantities R_1 and R_2. Suppose, I assume that both the intensities, by looking at the previous page if I assume that both the intensities I_0 $\text{lambda}_{\text{on}}$ and I_0

lambda$_{off}$ are the same if I am able to arrange that then ratio R_1 by R_2 is equal to I_L lambda$_{on}$ by I_L lambda$_{off}$. So the ratio of the numerators of in these two will also give R_1 and R_2. So, I am able to get the same intensity or adjust the intensities of both the radiation leaving to be the same value. Let us look at the schematic, and see what are the constituents of this particular measurement technique.

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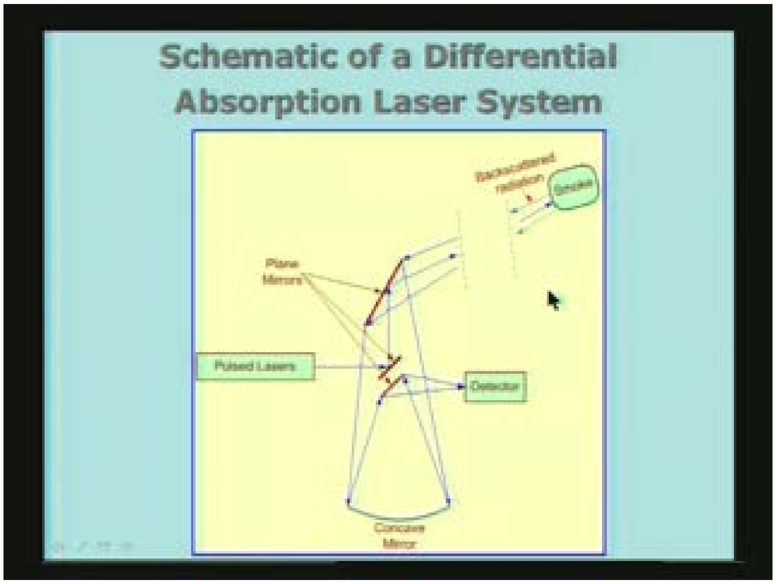

Schematic of a Differential Absorption Laser System

So we have a pulse of laser, in fact there will be pulsed lasers two lasers, one which is going to be lambda$_{on}$, and the other one lambda$_{off}$, so both of these pulsed lasers will be sent through the atmosphere. So in this case, I have made some arrangement there is a mirror and there is another mirror here so that the beam is sent in the direction of my interest. Pulsed laser means the laser is characterized by certain pulse width in terms of the duration and we are usually talking about very short duration pulse width and may be at a repetition rate which is few hertz. That means that the laser is sent again and again, so we can also measure the returning radiation again and again, and then average over several such pulses so that I can improve the signal to noise. I have two pulsed lasers which are now going in the direction, and here is where I have the gas whose concentration I have to measure.

Let us look at what we can to do. The light which leaves the pulsed laser takes a certain amount of time to travel up to this, and then it starts returning, it will start returning from here, and then it will go to the smoke, and some back scattering will take place if there is a cloud, or something like that and therefore it is going to return from here. So it takes certain amount of time for it to go and come back. So if I make the measurement of the return signal after a time delay, I can adjust this time delay such that, I can sample the region which I have shown you. So I will choose the time delay such that and also the time over which I am going to make the measurement I will do such that I can specifically find out what is happening in this particular region between these two dashed lines which I have shown.

So what happens in this case is, the return signal follows the path, the forward path then it comes back and it is gathered by a concave mirror. Usually it is in the form of a telescope, and it is gathered by a concave mirror, and then reflected and the two beams are going to be detected by the detector. Let us recapitulate, there are two pulsed laser two pulses with same pulse width and same intensity are generated here, it is sent through the atmosphere where I want to make the measurement of constituent of interest to us, it is reflected back by some object, may be you can even arrange some kind of target there which can reflect it may be a flying aircraft can reflect it and then it comes back, and is gathered by this concave mirror, because the return signal is very weak, the pulse which is going is very strong but when it returns only a small fraction will be returned, because it will be scattered into all directions, and the beam will be expanding and therefore the intensity is falling, and therefore what is coming back is a small percentage.

Therefore, in order to get a sizable signal, I have to gather a radiation over a large area therefore, I have a large concave mirror to concentrate all the radiation on to the detector. And the pulse duration and the duration between pulses are under my control and also the duration over which I can make the measurement is in my control. So, I can choose a certain window in between two pulses such that I can sample this region for example. Of course, this region can be shifted, accordingly the duration over which we are going to make the measurement.

So the pulsed lasers, then the return signal, the detector. The detector has to be very sensitive, because we are talking about very small intensities of the returning signal, and the detector must be capable of distinguishing one lambda from the other. So we must have a detector, or a detector pair which is going to measure these two, or of course these two pulses can be sent with a small time difference, and the detector can detect one after the other, and then the ratio can be taken.

Let us look at a typical example, a Lidar atmospheric sensing airborne water vapor measurement. In this case we are interested in making the measurement of water vapor in the atmosphere. The experiment is called LASE or L A S E for Lidar atmospheric sensing experiment, conducted by NASA. The amount of water vapor could be between 0.01 g per kg to 20 g per kg. Aerosol backscatter ratios can be measured from ground to 20 km. I am talking about the distance over which this measurement can be done and a resolution of 30 m.

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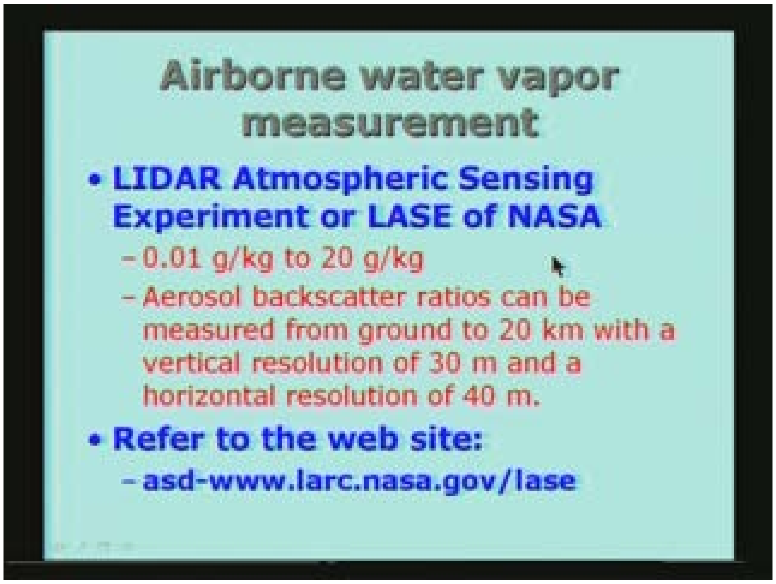

Airborne water vapor measurement

- LIDAR Atmospheric Sensing Experiment or LASE of NASA
  - 0.01 g/kg to 20 g/kg
  - 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.
- Refer to the web site:
  - asd-www.larc.nasa.gov/lase

I can decide the particular region in which I want to make the measurement, and the resolution is 30m vertically and horizontal resolution of 40m. That means I can choose the region over which I can make the measurement. Here are a few characteristics:

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LASE H_2O DIAL Parameters Transmitter

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

The energy of both the on and off laser beams is 150 mJ, that is the amount in each pulse, line width is 2.5 pico meter so the line width is very narrow, repetition rate is 5 Hz for every second there are 5 pulses which are transmitted, the wavelength is 813 and 818. So you see that, they are very close to each other just with a 5 nanometer difference. One of them is absorbed by the water vapor, the other one is totally transparent to water vapor. The beam divergence is 0.6 milli-radians; pulse width is 50 nanoseconds, so we are talking about very small and narrow pulse width and the aircraft altitude is 16 minus 21 km and the aircraft velocity is something like 720 km by hr or 200m per s.

In this case the measurement is done from the aircraft. The aircraft is going to make the measurement. What are the things required by the receiver? As you can see receiver has an area of 0.11m square which is a large area and the field of view is 1.1 milli-radian and the bandwidth is 0.4 nanometer during day time, and this measurement is done both during day time and night time.

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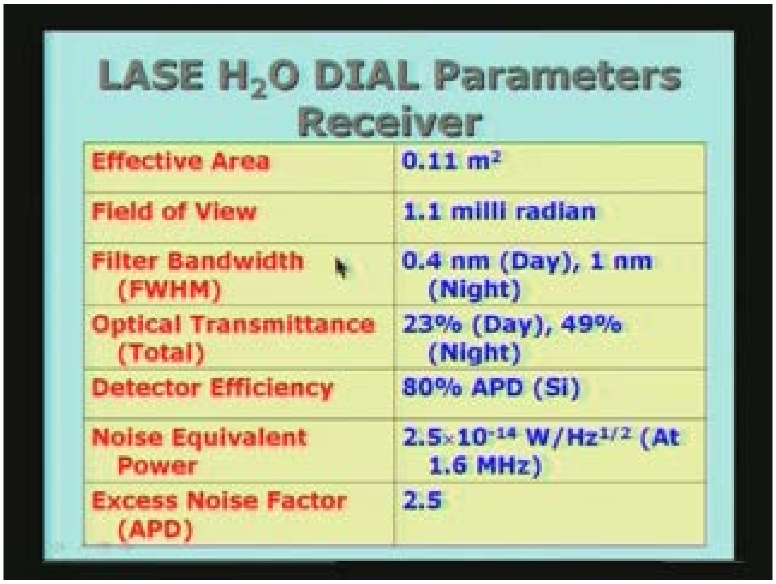

LASE H_2O DIAL Parameters Receiver

Effective Area	0.11 m^2
Field of View	1.1 milli radian
Filter Bandwidth (FWHM)	0.4 nm (Day), 1 nm (Night)
Optical Transmittance (Total)	23% (Day), 49% (Night)
Detector Efficiency	80% APD (Si)
Noise Equivalent Power	2.5×10^{-14} W/$Hz^{1/2}$ (At 1.6 MHz)
Excess Noise Factor (APD)	2.5

The optical transmittance values are given as 23% during day time, and about 49% at night time, the detector has 80% efficiency, the detector used is called avalanche photo diode and it is a silicon material basically with doping and it has got quantum efficiency of 80% so that is what detector efficiency means. The noise equivalent power is very small that means it is highly sensitive. The smaller the value which is given here the larger is the sensitivity and the excess noise factor is 2.5 for the APD. Just to recapitulate, what we are trying to do is to measure the ratio R_1 by R_2. The two pulses are sent through the atmosphere and then the concentration is pulled out from this, and the concentration values are already given in the specification. So the next technique I am going to look at is given here the chemiluminescence for NOx detection.

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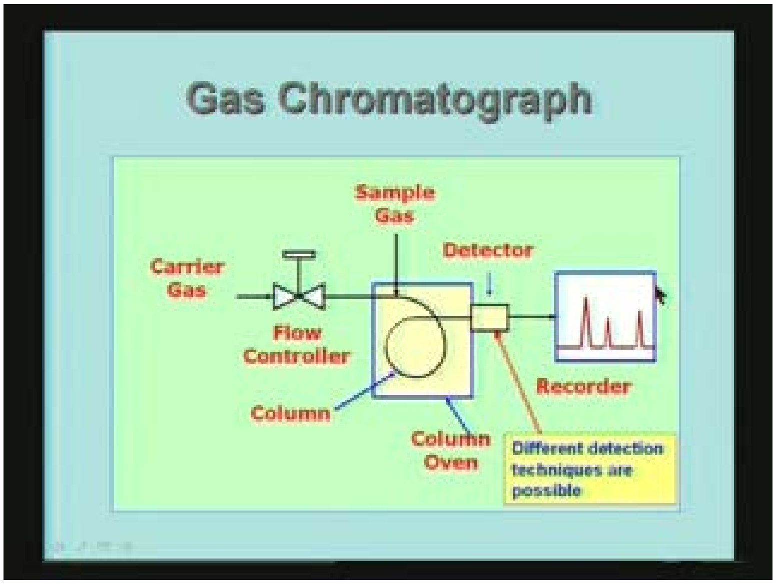

Gas Chromatograph

Sample Gas

Carrier Gas

Detector

Flow Controller

Column

Column Oven

Recorder

Different detection techniques are possible

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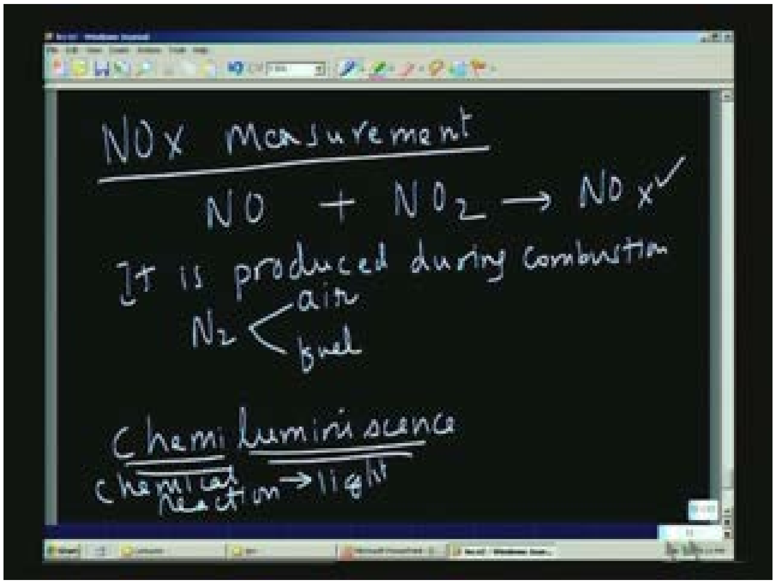

NOx measurement

$NO + NO_2 \rightarrow NOx$ ✓

It is produced during combustion

$N_2 <$ air, fuel

Chemiluminiscence

chemical reaction → light

What this NOx is?

Actually nitric oxide plus Nitrogen dioxide is referred to as NOx and it is produced in combustion devices during combustion. And for Nitrogen because Nitrogen oxides are formed Nitrogen either comes from air or it may come sometimes from the fuel also. Fuel might have some Nitrogen in it. But what we are interested in is measuring the NOx. So the method of measurement is called chemiluminescence.

What does it mean?
Chemi means chemical and luminescence means light. Chemical reaction gives rise to light so the chemical reaction is the reason for light. if I have a mixture of nitric oxide and Nitrogen dioxide what I can do is, I can convert this to NO, that means NO is already there is some NO_2 in the sample gas I want to convert everything to NO so that NO plus NO_2 is equal to NOx, so, I am converting everything to NO that means that when you convert the NO_2 to NO this is like equivalent to NOx.

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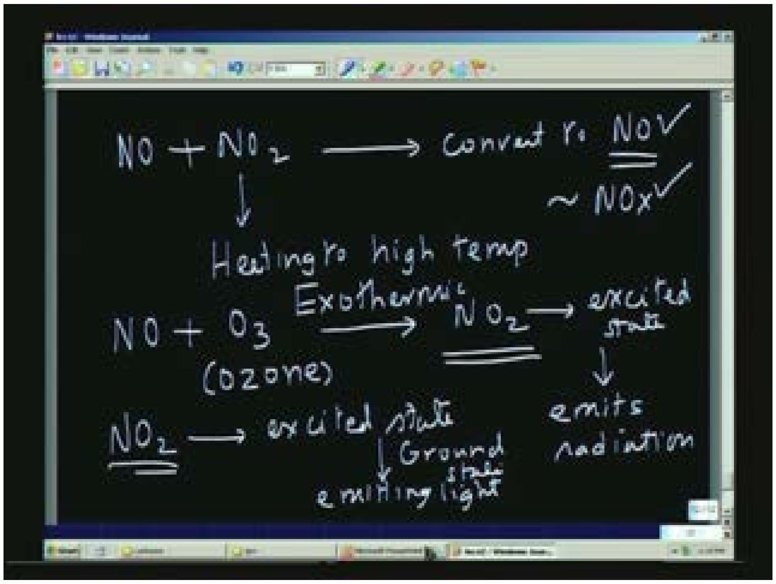

$NO + NO_2 \longrightarrow$ Convert to $\underline{\underline{NO}}$ ✓

$\sim NOx$ ✓

$\downarrow$

Heating to high temp

$NO + O_3 \xrightarrow{\text{Exothermic}} \underline{\underline{NO_2}} \longrightarrow$ excited state $\downarrow$ emits radiation

(ozone)

$\underline{\underline{NO_2}} \longrightarrow$ excited state $\downarrow$ Ground state

emitting light

So if I convert all the Nitrogen oxide to nitric oxide, this is reduction reaction, in NO_2 there are two Oxygen and in NO there is only one Oxygen so I have to reduce NO_2. It is done very simply by heating to high temperature. So if I heat to high temperature Nitrogen dioxide is converted to Nitrogen oxide. Even if I cool it subsequently, it does not become NO_2 again because it takes a long time for that to happen. Therefore, essentially if I perform a chemical reaction by just heating, I will get Nitrogen nitric oxide,and the first step is that I am going to take the mixture of NO and NO_2 and convert to nitric oxide so now I am going to find the method of measuring NO which is actually done in the following way. If I take Nitrogen oxide and if I react it with ozone O_3 I will get NO_2. Of course one will ask me why we converted NO_2 into NO and now we are again converting everything to NO_2.

The point in the first reaction is to convert everything so that you are going to measure directly the NOx. The second reaction is to produce NO_2 because in this the reaction which is taking place is exothermic and therefore NO_2 is in the excited state, and it emits radiation, and this emission of radiation is actually called the chemiluminescence. Therefore chemiluminescence is nothing but the emission of radiation by Nitrogen dioxide in the excited state.

How did it reach the excited state?
NO was reacted with ozone and because it is exothermic the reaction leads to Nitrogen dioxide and the Nitrogen dioxide is already in the excited state because of the exothermic reaction the high temperature the temperature goes up because of that and this emits radiation. Therefore finally we have, NO_2 in the excited state. Of course, not all of them will be in the excited state. At any particular temperature, there is equilibrium, the excited state will have a certain concentration. Certain number of these is going to be in the excited state, and they are going to jump to the ground state by emitting photons or emitting light of the characteristic frequency which is the infrared part of the spectrum.

In the excited state not all of them are going to come to the ground state, but some of them are going to come to the ground state, and during this process, certain amount of light is going to be emitted, and what I have to do is to measure the intensity of light which is emitted, and that can be related to the concentration of NO_2 which will be related to concentration of NOx, so we work backwards and go back to the NOx. This is one part of the story.

Suppose, we want to measure nitric oxide separately, and Nitrogen dioxide separately that also can be done, because at low temperature Nitrogen dioxide remains as Nitrogen dioxide and nitric oxide remains as nitric oxide. These two components are separately available. For example, I can measure NO_2 from here separately by some other method, it may not be chemiluminescence method so that I can measure NO and NO_2 separately, or you can use the separation methods.

So the chemiluminescence detector or the detection of NOx depends on the conversion of NO_2 to NO so that you get NO plus NO_2 mixture becomes NO completely, and then allowing it to react with ozone to form Nitrogen dioxide in the excited state, measure the amount of radiation coming out of the Nitrogen dioxide in the excited and relate it to the concentration of the Nitrogen NOx in the sample. This is the chemiluminescence method which is very often used in the laboratory. Chemiluminescence NOx measuring devices are available in readymade state and it is supplied by various manufactures and one can just buy it and use it. The total conversion from NO_2 to NO and the ozone and so on are done in the instrument. We have discussed non separation methods. In fact there are many other methods.

Let us look at the separation methods. There are two separation methods. One is gas chromatography, and the other one is Orsat gas analyzer. Let us look at gas chromatographic method of separation of species, and the measurement of these, by using a suitable detector. The method can be explained by the following kind of schematic. The gas chromatograph depends on several factors. One is we need a carrier gas.

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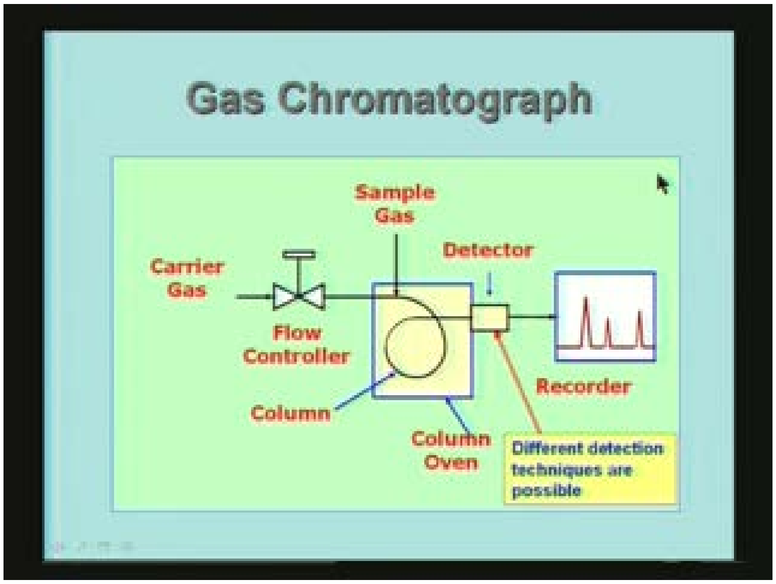

Gas Chromatograph

Different detection techniques are possible

For example, Helium, Hydrogen, Nitrogen, Argon, are all carrier gases which can be used. So the carrier gas is going to be mixed with, or the sample gas is going to be mixed with the carrier gas. So the carrier gas flow is controlled by using a flow controller here, and it is just a valve, and there is a source of carrier gas which is usually in the form of a cylinder containing high pressure carrier gas, and of course, there should be a regulator so that, I can send it in at the required pressure and it can goes through the flow controller, and the amount of flow is controlled by that one.

The sample gas contains the gases whose concentration I want to measure. That means that the sample must be collected somehow, and it must be brought to this place, and it must be mixed with the carrier gas. So what happens after that? At this point we have the mixture of sample gas, and the carrier gas and it goes through what is called a separation column. Let us assume that it enters the separation column which is shown here schematically by this loop. In practice, this loop consists of several meters of small narrow tube which is referred to as the capillary, and the capillary has got either porous layer inside of the tube, or it could be coated with some material which absorbs the gases. So it is nothing but adsorption.

Adsorption means the gases have a tendency to stick on to the wall. If it is porous also it will go through the pores and it will get struck there. And what happens is when you send a mixture of gases and the carrier through that the carrier keeps continuously flowing because the carrier is always there and a small amount of sample is allowed and it is stopped.

Now, in other words you are introducing a small amount of sample into the carrier gas. So carrier gas is moving all the time and a small pulse of sample gas is introduced, and what happens to the sample gas is the sample gas may consist of several components, some of the components may be easily adsorbed but some of the components may be difficult to adsorb. So, depending on the their capacity to adsorbed by the surface they will migrate through this separating column, even though it is not in the form of column it is called as column it is in the form of a loop here it is a column because on the inside it looks like a column, because it is a very long one and when the sample gas moves through that, the different constituents in this sample gas will move through this column at different velocities. That means, at the other end of the column the one which moves faster will come first here, and the one which moves a little slower than that and the one that is slower to that and so on.

Therefore, if you look at the gases coming here, it will be carrier gas plus the one which moves at a fastest speed will come first, and then after a gap the next one will come, because we have introduced a sample which is in the form of a pulse so the first one to come will be the gas which moves faster through the column, and after sometime the next gas will come and so on. So what happens is, by the time when you come here, the gas is coming as separated species. So, if I have a detector here, it detects the presence of the gas other than just the carrier gas. So there must be some difference between the carrier gas, and the sample gas or the constituent which I am interested in which should be detected by the detector. That means the carrier gas has some property, the sample gas must have the same property but with a slightly different magnitude. So, the detector will now sense the presence of different species, and if you record the species coming out it is first the lightest gas and then the heavier gas and so on and so forth.

What you are seeing here is, a chromatograph the axis here is time, and what you see here is, the concentration of the gases the one which came first, the one which came next and the one which came subsequently and so on so they are separated as peaks here. So the area under this peak is proportional to the concentration of the gas in the sample. There are different ways of detecting the gases as they come out of the system.

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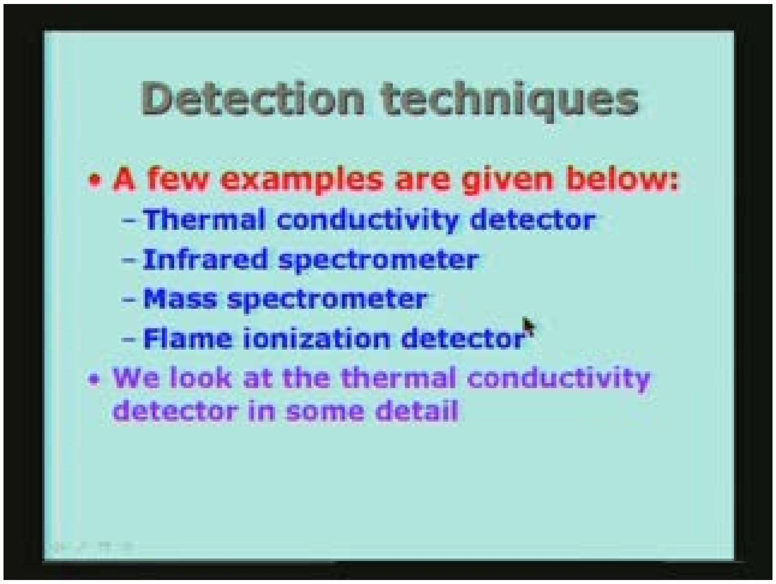

Detection techniques

- A few examples are given below:
  - Thermal conductivity detector
  - Infrared spectrometer
  - Mass spectrometer
  - Flame ionization detector
- We look at the thermal conductivity detector in some detail

Therefore different detection techniques are possible. Here are a few examples. For example, here is the thermal conductivity detector. I can use the infrared spectrometer. We discussed about spectrum of various gases, they have specific bands in which they will absorb therefore if you use an infrared spectrometer by finding out where the absorption is taking place, I know what gas it is and also by measuring the amount of absorption I can immediately say what the concentration is.

Relating it to the Beer’s law it states that the absorption is exponential so the amount of absorption is exponential and depends on the concentration and the path length. So exactly the same thing can be applied if you use an infrared spectrometer which can measure the gas concentration then we can use a mass spectrometer. Mass spectrometer is where you measure the weight or the mass of the species and mass spectrometer will separate out the species in terms of their masses. It is actually much more complex than what I am trying to infer.

Mass spectrometer can be used in principle or you can use what is called a flame ionization detector. So this will again give a characteristic emission and just like in the case of chemiluminescence detector the light emitted can be used for detection. Let us take one detector which is very easy to understand, and we will look at the thermal conductivity detector in some or more detail than the other cases. So the infrared spectrometer or the mass spectrometer are advanced techniques, and they can be used, and mostly these are used when you want a very fine measurement involving very low concentration.

Thermal conductivity detector is useful when the concentration is not very low but infrared spectrometer or mass spectrometer and so on can be used when the concentration is extremely low. Very trace amounts are present, We can determine using the spectrometers of various kinds. Let us look at the thermal conductivity detector in some detail and that requires a little background on the process which may take place. So, if you look at gases different gases have different thermal conductivities, this is a very important observation. Some gases have higher thermal conductivity than others. Let us look at some of the typical gases which we meet with in practice.

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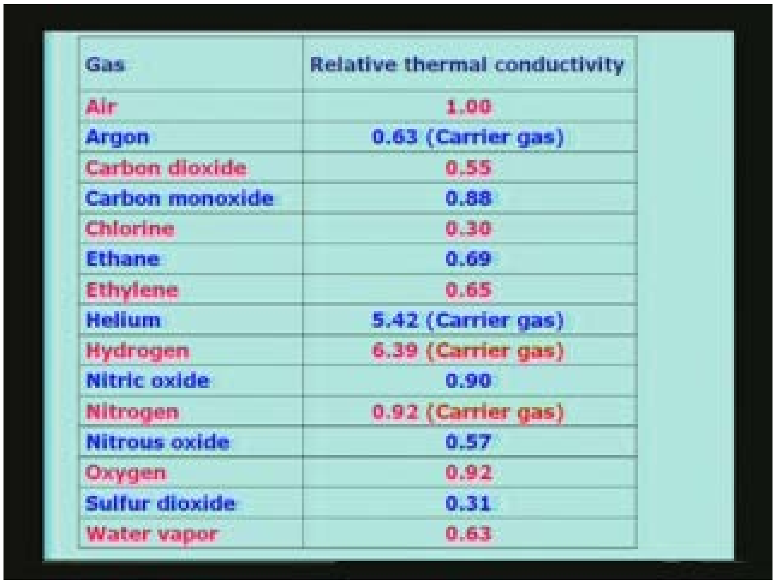

Gas	Relative thermal conductivity
Air	1.00
Argon	0.63 (Carrier gas)
Carbon dioxide	0.55
Carbon monoxide	0.88
Chlorine	0.30
Ethane	0.69
Ethylene	0.65
Helium	5.42 (Carrier gas)
Hydrogen	6.39 (Carrier gas)
Nitric oxide	0.90
Nitrogen	0.92 (Carrier gas)
Nitrous oxide	0.57
Oxygen	0.92
Sulfur dioxide	0.31
Water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

For example, if I take air as 1.00 so whatever is the thermal conductivity of air, I will just take it as the basis. Actual thermal conductivity of air is about 0.025 W by mKelvin but here I am making it 1. So what I am trying to do is to find out the relative thermal conductivity of different gases with respect to air. So, if air has got thermal conductivity of 1, then what is the thermal conductivity of other gases in terms of air thermal conductivity?

This is the ratio. For example, if I take argon, it is less conducting than air it is about 0.63, carbon dioxide is 0.55, all these are at one temperature may be at 0 degree Celsius or 25 degree Celsius, usually either 0 or 25 degree Celsius is quoted and carbon dioxide is 0.55.

Carbon monoxide is having higher thermal conductivity, and therefore it is 0.88 it is closer to air, than carbon dioxide. Therefore, because these two have different thermal conductivities, I can distinguish carbon dioxide and carbon monoxide if I can have a detector which will detect the difference between the thermal conductivity, and that is the basic idea. Chlorine is 0.3, ethane is 0.69, ethylene is 0.65, here this is used as the carrier gas helium, it has a extremely high thermal conductivity of 5.42, so it is five times as air is so 5, if you take hydrogen it is even more or so. You will also notice one thing that, the lighter the gas is, the smaller the molecular weight, the higher the thermal conductivity.

For example, helium, hydrogen is a very light gas, it has got a very high thermal conductivity it has got 6.39 as compared to 1 for air, Nitric oxide is 0.90 and

Nitrogen is also used as a carrier gas. Actually what is the difference between air and Nitrogen? Air contains a large percentage of Nitrogen and some small smaller percentage of Oxygen. And if you see here Oxygen is also more or less like 92 more or less like that. Of course, air may contain other constituents therefore, it is equal to 1. So Nitric oxide is 0.9, Nitrogen is 0.92.

Of course if you see here Nitrogen and Oxygen I cannot distinguish using thermal conductivity, because they have more or less the same thermal conductivity. Therefore, Oxygen cannot be monitored using the thermal conductivity as the basis. Nitrous oxide is 0. 57, Sulfur dioxide is 0. 31 and water vapor is 0.63. And why I have included water vapor is that in most combustion devices water vapor is also present in the form of steam or water vapor therefore that is also of interest to us. So let us see how we can use this information.

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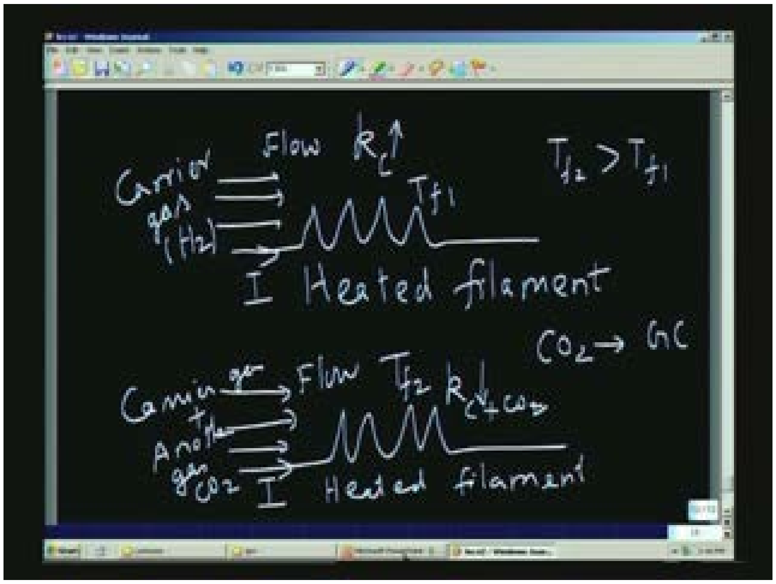

Actually, we have come across this thermal detection earlier, when we are talking about pressure transducers we have actually discussed some of these issues. Just to recapitulate I am trying to look at it again. So, I have a heated filament that means I am passing a current through that, and now I make the gas flow across that. Let us make one more sketch, identical filament and, I have the identical current I am having another flow here, and let us say this is the carrier gas, one of the gases which we had, for example, I can have helium or hydrogen just to take as an example, and here carrier gas plus another gas, for example, carbon dioxide.

So, I have a small percentage of CO_2 being carried by the carrier gas, and let us say that this CO_2 is from the gas chromatograph. So, I have a sample of gases taken in some particular application, and I have sent it to the gas chromatograph, and at certain times the gas coming out is actually a mixture of carrier gas and CO_2. So, the carrier gas for example, hydrogen has a very high thermal conductivity. But, if I put a small amount of CO_2 into it, the thermal conductivity will come down, and therefore this k is higher and k is lower here. The k here is higher than the value here. Suppose, I say this is k carrier plus CO_2 this is lower than this.

Therefore the heat transfer from the heated filament to the flow assuming that the flow is identical the same flow rate, and I am assuming that the flow is maintained more or less identical, the passages are the same then the heat transfer from the carrier gas CO_2 mixture will be smaller than that in the case of carrier gas alone. Therefore, there is a small change in the heat transfer. Therefore, if I am having the same current, and so on this filament will tend to heat up so the temperature of this T_{f2}, this is T_{f1} so T_{f2} will be greater than T_{f1}. Suppose, these two filaments are made part of a bridge circuit then, if both of them have carrier gas passing around them they will be having the same resistance, and therefore they will be balanced. So when I have a gas consisting of carrier plus CO_2 or carrier plus another gas, and in this case carrier only there is a slight difference in temperature, because of the heat transfer rates being different for two filaments.

Therefore, it is because the temperature changes, and because the resistance of the heated element is dependent on the temperature it is just like a RTD or resistance temperature detector, the temperature changes and because of that the resistance will change and because the resistance changes the bridge will go out of balance and the out of balance voltage which is a small value can be amplified, and it is proportional to the concentration of the CO_2.

Let us look at the how it is going to come out. Let us look at the schematic of thermal conductivity of a mixture of hydrogen and carbon dioxide. So, if I put percent of hydrogen in the mixture in the x axis and the thermal conductivity in W by m degree Celsius, you see if the percentage of hydrogen is zero that means all CO_2 the value is around here 0.015 something like that, and if I go to 100% hydrogen then it is all 0.17 or 165 or something like that.

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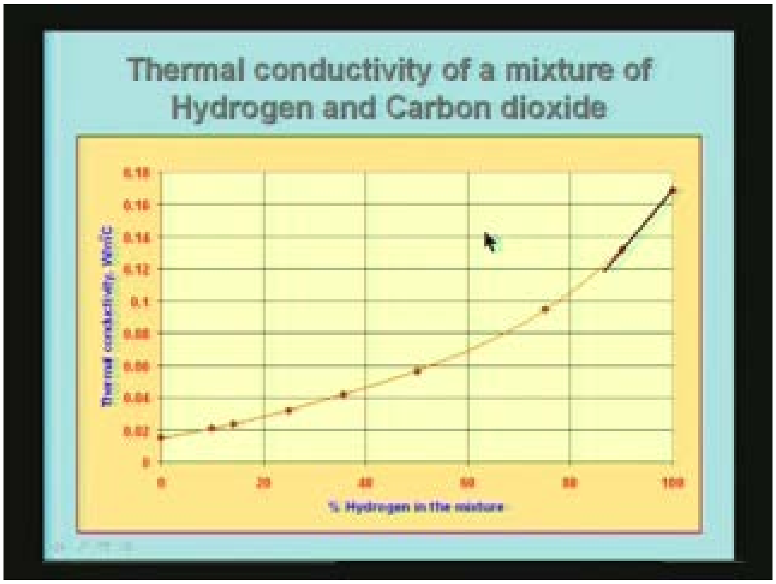

Thermal conductivity of a mixture of Hydrogen and Carbon dioxide

So, if I draw all these data which is available, and if I pass a curve you see that it is very close to 100% hydrogen. That means I have a small percentage of carbon dioxide in the mixture it is more or less linear. That means that the thermal conductivity change between the carrier gas and the carrier gas plus CO_2 which I was talking about earlier, is a small amount and in that range I can use a linear relationship between the thermal conductivity and the percentage of CO_2 in the mixture because 100% hydrogen here means, it is 80% here and 20% carbon dioxide.

In other words, I can say that 100 minus whatever value that gives you the percentage of CO_2 here. If it is 95%, that means 5% CO_2 so the thermal conductivity comes down very slightly. That means that the resistance or the temperature is going to change by a small amount, and if we have sensitive detection we can determine or detect this temperature difference in terms of change in the resistance, and this change in resistance can be monitored and related to the concentration of the CO_2 in the mixture.

Let us see how it is going to be done in a thermal conductivity detector. The schematic is shown here. The thermal conductivity detector consists of four identical heater wires, and this whole thing is put in a block and the block is kept at a uniform temperature.

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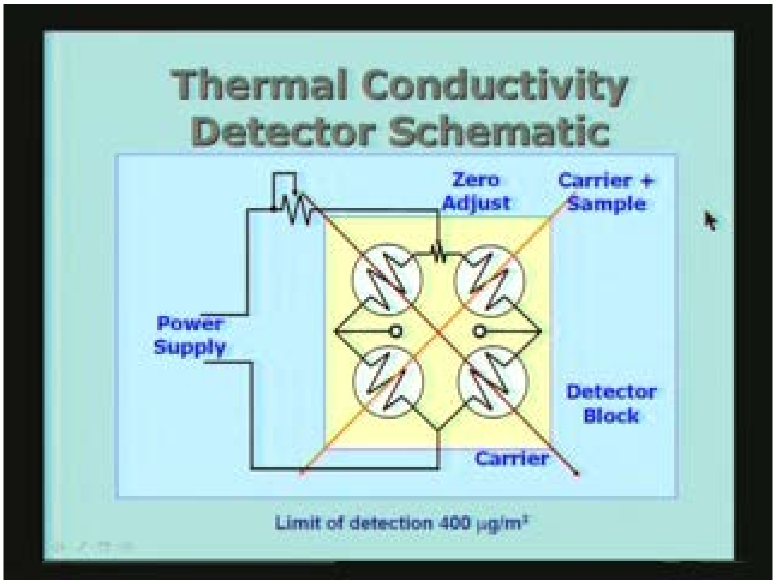

Thermal Conductivity Detector Schematic

Limit of detection 400 $\mu g/m^3$

All the four detectors are in a block, and the block is maintained at some constant temperature. Now I have the carrier gas passing through these two heater elements, and the other two heater elements are going to be exposed to carrier plus sample. Sample means in this case we are talking about CO_2. It may be any other gas which we are trying to ascertain the concentration on. So we have the carrier plus sample going through these two and they are in the opposite sides of the bridge circuit, or the Wheatstone bridge circuit and these two are on the other side of the Wheatstone bridge circuit. These two are exposed to carrier gas alone, and these two are exposed to carrier plus sample gas and at the outside whatever I have shown in this yellow background is actually an isothermal enclosure or a block.

Why do we have an isothermal block?

We have four heaters, two of them exposed to the carrier gas, and what happens to the heat generated by the filament it has to be transmitted from the filament to the block. So the block temperature is not changing, and the block temperature is constant. Therefore the amount of heat transfer from the filament to the block will depend on the temperature of the filament. Therefore if one of the filaments is at higher temperature, more heat will be lost from there. But the block itself will be at almost constant temperature, because it is a very heavy mass which is maintained at a constant temperature. Therefore it provides a heat transfer environment for the detector. So, these two which are exposed to the carrier gas will be at a slightly lower temperature with respect to carrier plus sample.

If you add the sample to the carrier reduces the thermal conductivity of the mixture. The carrier if it has got a very high thermal conductivity, and the sample gas has got very low thermal conductivity it will reduce. In other words, if the carrier gas has a low thermal conductivity and the gas you are going to add is going to have higher thermal conductivity it can be in the other direction. But here, we took the case of helium or hydrogen they have very high thermal conductivity with respect to other gases, and therefore we are expecting the carrier gas plus the sample to have a lower thermal conductivity, and therefore these two filaments will be at slightly at higher temperature and immediately you see that an imbalance will be set up between these two terminals, and an imbalance voltage will appear here and there are some other adjustments here called zero adjustments.

Because, all these four may not be exactly identical so their zero adjust is made here so that we can take care of the adjustment. When all the four elements are exposed to carrier gas, then there should be exactly zero output here, so this can be adjusted by zero adjust here. And the power supply you can see here, I have shown some moving contact here the voltage which is impressed on this point and this point can be varied to suit the requirement. The essential part is that these four detectors which are put in this particular fashion two exposed to carrier and the other two exposed to carrier plus sample they are on the opposite sides opposite arms in the bridge and therefore it actually amplifies the difference. The voltage difference between these two points is twice, if it were not in this particular fashion.

So we are going to get a larger imbalance, and this is to be detected and the limit of detection is about 400 micro gram per m cube. This is the typical number. Let us see what we expect in the case of a GC detector.

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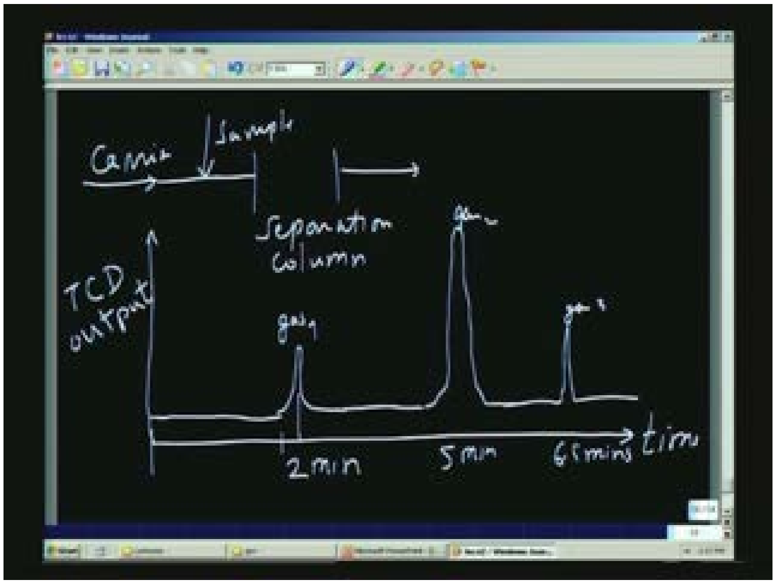

GC is assumed to be arranged like this. They have the carrier, this is the sample then it goes through the separator or separation column, and then what comes here are different gases, and therefore, if you look at the output, this is the time axis and this is the TCD output. TCD is Thermal Conductivity Detector output. Initially, it is only the carrier gas, and therefore, there will be no output, and after sometime, the first gas which is going to separate is going to come out, and it will give you a peak like this. So, this is gas 1, and then there will be no activity for sometime, and after sometime you will see that there will be one more peak that is gas 2.

Of course, the height of the peak, and the area under the peak will be based on the amount of the gas present, and after sometime again you will get the gas 3 and so on and so forth. This may be after two minutes, this may be after five minutes, and this may be after 6.5 minutes, and so on, and so forth. So, the gases come out of the gas chromatography column spaced in time. That means this is the initial time at which you are going to introduce the gas to the column, this is when we introduce the sample and then after two minutes the first gas will appear, and a small concentration is present. Of course, the gas concentration depends also on thermal conductivity ratio.

So we have to correct for the thermal conductivity of the particular species, or we can do the following. We can calibrate the instrument with different mixtures with different gases, and find out what is the output for a particular gas, and accordingly we can find out what is the scale factor for that particular gas and then introduce that in the quantitative interpretation of the signal. If you just look at the peaks all you know is that these gases are present. If you want to quantify this then the thermal conductivity of the gas must be known, and how it affects the TCD output also must be known, so that we can calibrate with different mixtures and these mixtures are readymade and available from manufactures so that you can use them for calibration.

For example, if I want to calibrate for CO_2, I must have carrier gas plus certain known fraction of CO_2 may be two or three different concentrations and use that, and calibrate the instrument so that I can get quantitative measurement that is possible of the gas concentration using the known gas concentration in the gas which is gas mixture supplied in a pure form. And of course, purity is very important because, if it is impure the idea of calibration will become meaningless. Just to recapitulate what we have done in the lecture today, the first technique look at was remote sensing and remote sensing of particular species of interest to us which was done by using a Lidar.

And you know Lidar is also used for ranging, range finding or finding the distance between a station and an object in which you are interested. So how it is done? It is done by finding out how much time it takes for the signal which leaves the Lidar to return. So the time difference between the forward emitted laser, and the return signal that can be linked to the time. The time between these two pulses can be linked to the distance, because we know that the speed of the light in the atmosphere is more or less like equal to 3 into 10 to the power m by s that is the speed of light. So we can find out how long it takes to go and come back, and therefore we know how to calculate the range.

Lidar is simply to determine the range of a particular object from the ground level or wherever you have situated. In other words, what I am doing is I am trying to find out the time. The time contains the distance information and the change in the intensity contains the concentration information. That is how you separate out the location we talked about some 20 m or whatever that means over that 20 m which can be situated at different distances from the Lidar. So we can determine the concentration in certain locations specifically determined by the ranging part of the Lidar.

The dial consists of Lidar and also the differential absorption and that is how you do that. Subsequently, we talked about the gas chromatograph which separates them into gases and they come out of the instrument at different time lengths and by Thermal Conductivity Detection we can find out how much is the concentration of a particular gas of interest to us. We also talked about NOx analyzer which is specifically a chemiluminescence method. Thank you.