Modern Instrumental Methods of Analysis

Prof. J.R. Mudukavi

Department of Chemical Engineering

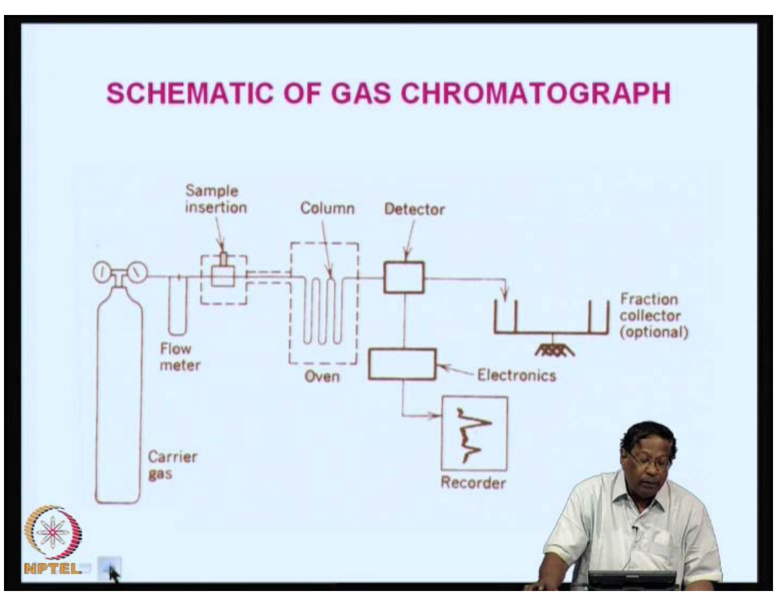
Indian Institute of Science, Bangalore

Lecture No. # 42

Gas chromatography-2 Applications

Welcome to the third class on chromatography, in the previous discussions we have we have studied about the chromatographic techniques in general and then gas chromatographic instrumentation followed by a discussion on the columns and now we will continue our discussion on the detectors.

(Refer Slide Time: 01:00)



Now, if you remember the slides what I had shown in the last class that is regarding the gas chromatography you can see in this slide that we have a detector attached to the end of the column and this detector senses the arrival of the systems and we would like to continue our discussions on what are the different types of discussions, detectors we are going to need them.

(Refer Slide Time: 01:38)

9. Detectors

Detectors sense the arrival of the separated components and provide a signal. These are either concentration dependant or mass dependant. All detectors are characterized by linear dynamic range (LDR - largest signal / smallest signal). Signal to noise ratio is 2 for the smallest signal. The detector should be close to the column exit and correct temperature to prevent decomposition.

So, in general the detectors sense the arrival of the separated components and provide a signal they these are either concentration dependent or mass dependent; that means, as the concentration of the gas carrier gas changes when the separated component enters the detector, the concentration will change and the concentration will increase to maximum and then it will slowly decrease.

So, it is either a concentration dependent or it can be mass dependent, because when we use hydrogen or helium gas any component that we are trying to separate would be heavier than hydrogen or helium or even nitrogen for that matter. If, you are using nitrogen as a carrier gas therefore, the detector can be mass dependent also. So, all the detectors in general are characterized by what is the minimum and maximum range.

What is the optimum range through which the sample can be analyzed this is known as linear dynamic range LDR. So, these are the actually LDR also represents largest signal divided by the smallest signal therefore, signal to noise ratio should be approximately 2 for the smallest signal therefore, the detector should be close to the column exit and the accurate temperature also must be also maintained to prevent decomposition.

(Refer Slide Time: 03:40)

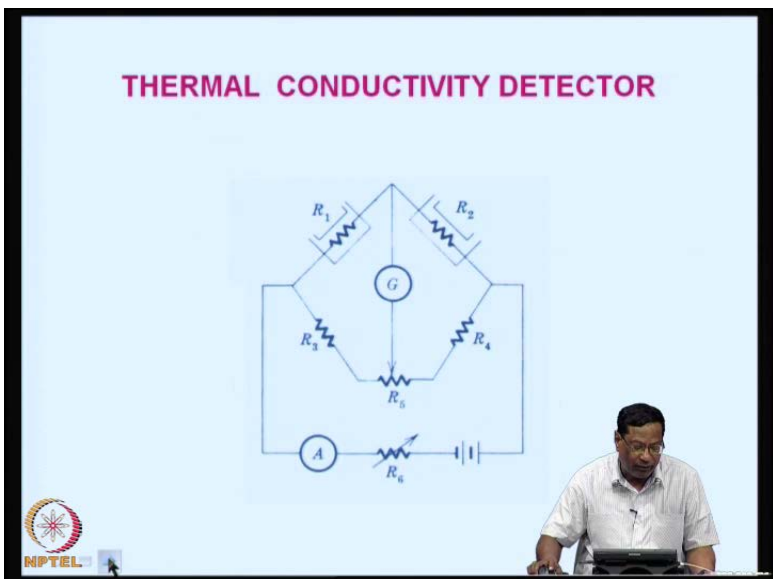
(i) THERMAL CONDUCTIVITY DETECTOR

It consists of 4 heating elements located in a heating cavity of brass or steel block which serves as a heat sink . Thermistors or resistance wires are used with Pt-Ir springs. Filaments are gold sheathed tungsten or teflon coated tungsten with high temperature coefficient of resistance. The cell cavity has 2.5 ml capacity for large TCDs or 0.025 ml for micro TCDs (5 ml).

So, if you take a look at the next slide we are going to discuss about the thermal conductivity detector. Actually, it consists of just 4 heating elements located in a heating cavity of brass or steel block which serves as a heat sink thermistors or resistance wires are used with platinum iridium springs and filaments are gold sheathed in a gold cavity their tube and the filaments are gold sheathed in tungsten or teflon coated tungsten also you can use with high temperature coefficient of resistance.

The cell cavity, the actual cavity in which the sample enters is approximately 2.5 ml for large thermal conductivity detectors or 0.025 milliliter for micro TCD's that is 0.025 milliliters or micro TCD's. So, the total volume could be maximum 5 ml of the whole TCD.

(Refer Slide Time: 04:59)



Therefore, the system is very simple like this that as I told you these are different resistance wires and then there is a galvana meter and then there is a resistance in one ampere meter and then one ammeter and this is the power supply. So, whenever there is a balance; that means, when the sample is not coming all the 4 arms of TCD are balanced therefore, there will not be any signal, the moment sample comes in there will be imbalance in 2 parts and the the remaining references will remain same, because there is no sample in that.

(Refer Slide Time: 05:52)

Thermal conductivity of the carrier gas and sample + carrier gas is measured. The TCD cells are connected to form the arms of a Wheatstone bridge. When pure gas passes both reference and sample wires are cooled to the same extent. When the solute emerges, the rate of cooling in the sample changes and the Wheatstone bridge is out of balance. This is recorded as a peak. Both He and H are useful as carrier gases since their thermal conductivities are different from the sample components.

NPTEL

So, this imbalance is recorded as a signal this is a very simple and straight forward concept and very useful also for the general materials; that means, it is not chemical specific detector. It is a general detector any substance that you are trying separate will is going to give you a signal, because when the sample enters the detector that filament signal it its job is just to cool the temperature, the wire temperature of the wire. So, thermal conductivity of the carrier gas and sample plus mixture is what we really measure.

The TCD cells are connected to form the arms of Wheatstone bridge as I showed you here like this, the Wheatstone bridge arms and when pure gas passes both reference and sample wires are cooled to the same extreme; that means, only when the carrier gases is being passed through they will be cooled to the same extent when the solute emerges out of the column and enters the the detector the rate of cooling in the sample changes and the Wheatstone bridge is out of balance this is recorded as a peak.

Both helium and hydrogen are useful as carrier gases whenever you are using thermal conductivity detectors. Since, because the thermal conductivities of hydrogen and helium are much different from the sample components, that is why? It is known as a common detector irrespective of the nature of the chemical species that you are trying to separate.

(Refer Slide Time: 07:46)

(ii) GAS DENSITY DETECTOR

The sample and carrier gas are split into two streams, where cooling is monitored. Two flow meters B_1 and B_2 are installed into the stream and are wired in a Wheatstone bridge. The reference gas enters at A, splits into two and exits at D. The effluent enters at C, splits into two mixes with the carrier gas and exits at D. The effluent does not come into contact with detector elements and hence no contamination and carbonization. But it takes the path AB_2D with a temperature rise in B_2 and decreases in temperature of B_1 in AB_1D. The bridge imbalance is recorded as a signal.

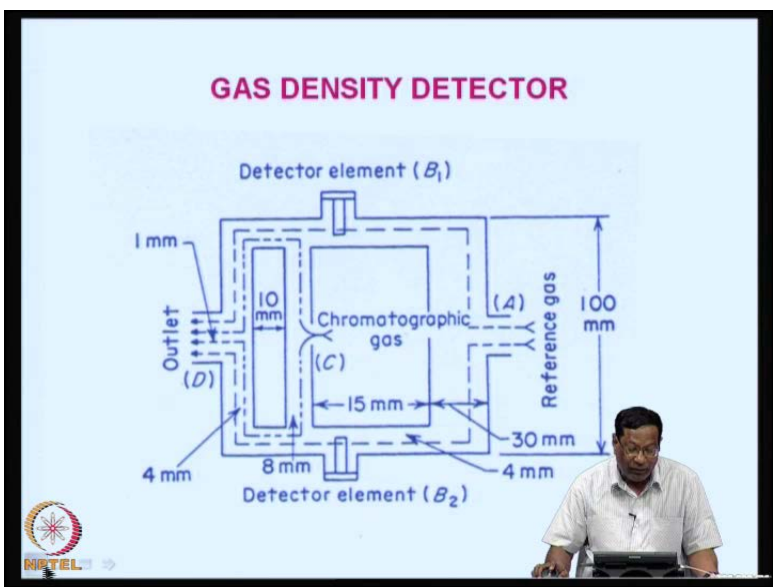
The detector accommodates a sample volume 5 ml sample volume of 5 ml, operating temperatures of 100-300^0 C.

NPTEL

Now, I want to discuss with you about the gas density detector; gas density detector actually is a very simple arrangement like this that you can see the in this figure the size

of the detector is approximately just 100 mm that is 10 centimeter and the reference gas enters like this.

(Refer Slide Time: 07:50)



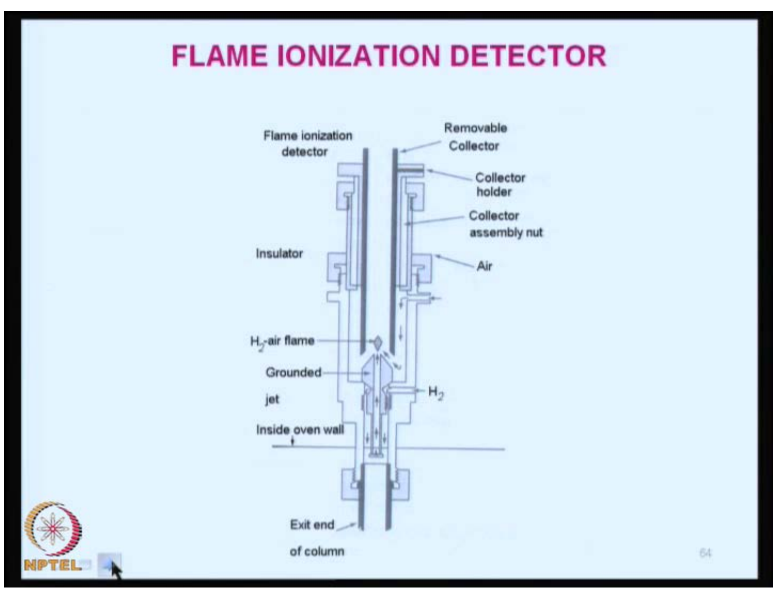
And then this is a solid block as therefore, the reference gas has can take can take the path either like this and then goes out or it can take a path like this and then go here and then comes out. The gas the chromatographic components will enter through this block and they have, they can also enter through this and go up like this and come out mix with the carrier gas here or it can come down and go here therefore, what is happening in this case is both the carrier gas and the sample gas are coming out and getting mixed. So, they are split basically into two streams the where the cooling is monitored.

Two flow meters we have shown that is B 1 and B 2 in the previous slide they are installed into the stream and are wired again in a Wheatstone bridge, the reference gas enters the reference gas enters at a in the when it is passing through A B and I call it D A, B D or it can come like this a and then B 2 D, A B 1 D and A B 2 D both both possibilities are there and I have a flow meter B 1 and B 2 here.

So, when I have the reference gas it splits into two end exits at the point D, the effluent enters at C again splits again into two mixes and mixes with the carrier gas and exits at D, the effluent does not come into contact with the detector element and hence there is no contamination and no carbonization, but it takes the path it can take either A B 1 D or A B 2 D that is one from the top or one from the bottom.

That is only two parts are there. So, that it generally whenever carrier gas enters it will take the path from the bottom preferably, because any of the chromatographic component you want to separate is heavier than the carrier gas. So, it will take the path A B 2 D with a temperature rising B 2 and decreases in the temperature of B 1 that is A B 1 D and the detector it goes either preferentially A B 2 D like this instead of A B 1 D.

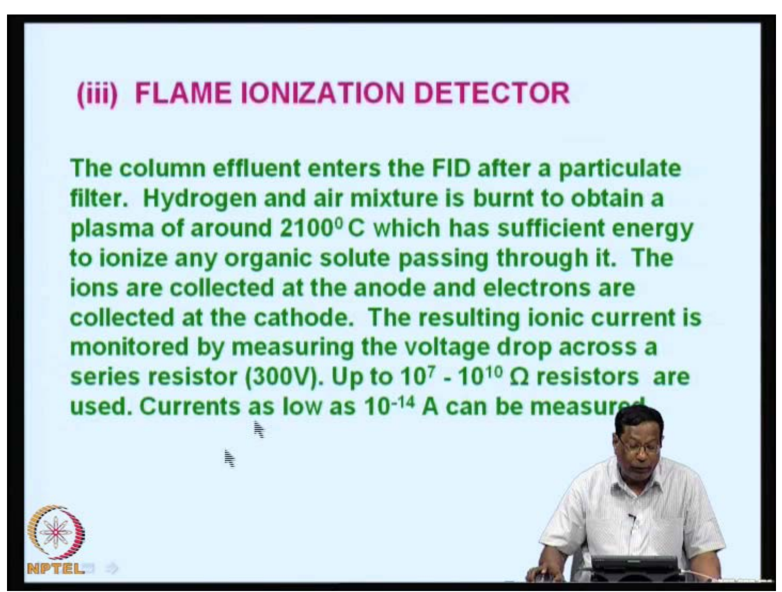
(Refer Slide Time: 11:36)



So, this is the basic principle of the gas density detector again I have to emphasize that it is a universal detector. So, the bridge imbalance when the sample enters is recorded as a signal, the detector accommodates a sample volume of maximum 5 ml and a 5 ml sample the operating at temperatures of about 100 to300 degree centigrade we can operate it.

Now, I want to talk to you about another detector that is flame ionization detector this is slightly more complicated and I am showing you a schematic diagram of the FID; that is flame ionization detector. Here, what I have is this is the oven wall and then this is the exit end of the column it is connected directly to a tube and there is a hydrogen entering a stream of hydrogen is entering into this tube and mixes with the sample and here it is lighted to make the hydrogen, air flame and then we have other paraphernalia like this insulator there is an air inlet collector assembly nut etcetera.

(Refer Slide Time: 13:38)



And here when the flame is ionized I have a collector here, one is removable collector and there this is a collector holder and flame of FID flame of ionization detector, the basically the whole idea is to put a to put a wire in which the sample ionizes and the wire will collect the ions and then generate some amount of current therefore, the column effluent enters the FID after a particulate filter we do not need, the particulates in that it is a very important component of a flame ionization detector.

So, other aspects include hydrogen and air mixture to be burnt to obtain a plasma of about 2100 degree centigrade which has sufficient energy to ionize any of the organic solute passing through that, the ions are collected in the anode and electrons are collected at the cathode the resulting ionic current is usually monitored by measuring the voltage drop across a series of resistors up to 300 volts and then the resistors are of the order of about 10 raise to 7 to 10 raise to 10 ohm's and currents as low as 10 raise to minus 14 amperes can be monitored.

That means this is going to be this is a very very sensitive detector as far as gas chromatographic detectors are concerned, the only requirement in this case is the material should burn when their separated sample component must burn giving you a large number of ions and electrons at the plasma temperature of about 2100 degree centigrade.

When the solute is burnt basically a large increase in the electrical conductivity is seen due to the number of carbon atoms. The detector is usually insensitive to water permanent gases do not generate any ions and inorganic components usually do not carbon monoxide no, carbon dioxide no, because they cannot generate the ions and it therefore, it is usefully for organic compounds contained in aqueous solutions also and it is useful for air pollution studies.

But, current decreases usually for substituted amines, halogens, OH groups etcetera, the linear dynamic range that is the ratio of the largest signal divided by the ratio of the smallest signal is about 10 raise to 6 therefore, the FID is a very good detector and again a general detector for organic compounds except the things what I have mentioned here that is water, CO, CO 2 and permanent inorganic gases, permanent gases etcetera.

And the current also decrease. Because, if there are amines etcetera. A sample splitter is therefore necessary in using a FID precise temperature control is not a rigid requirement, because when you are attaining temperatures of about 2100 to 2200 degrees it does not make much sense in maintaining the temperature exactly around that temperature.

FID is in general, insensitive to what are permanent gases such as CO, CO 2, carbon disulphide, sulphur dioxide, hydrogen sulphide, ammonia, nitrous oxide, nitrogen oxides, nitrogen dioxide, silicon tetra fluoride, silicon tetra chloride, etcetera therefore, it is an advantageous in moist air samples for the analysis of organic components.

(Refer Slide Time: 17:51)

FID is insensitive to water and permanent gases such as CO, CO_2, CS_2, SO_2, H_2S, NH_3, N_2O, NO, NO_2, SiF_4, $SiCl_4$ etc. Therefore it is advantageous in moist air samples for the analysis of organic components. CO and CH_2 get converted to CH_4 over nickel catalyst and the sensitivity is 5 ng / sec^{-1}. For higher organic gases the sensitivity is 10 pg / sec^{-1} . LDR is 7.

That is why? I was trying to tell you that it is good for the air pollution studies, because permanent gases do not give you any signal. So, any organic compounds that are present in the air they can be absorbed or taken up in a aqueous solutions and then pass through the g c and then they will give you a signal carbon monoxide and CH 2 are some of the components they get converted to carbon, methane in general if you pass it over a nickel catalyst place some in the way in FID.

And the sensitivity of such determination is 5 monograms per second for higher organic gases the sensitivity is 10 pikograms per second, the 10 pikograms per second is a fantastic sensitivity the linear dynamic range for FID is about 10 raise to 7 that makes it one of the best detector available in the gas chromatography. Therefore, usually 99 percent of the gas chromatographic equipments will have TCD or FID, thermal conductivity detector for general separation of the components of general character and FID for organic substances.

(Refer Slide Time: 20:15)

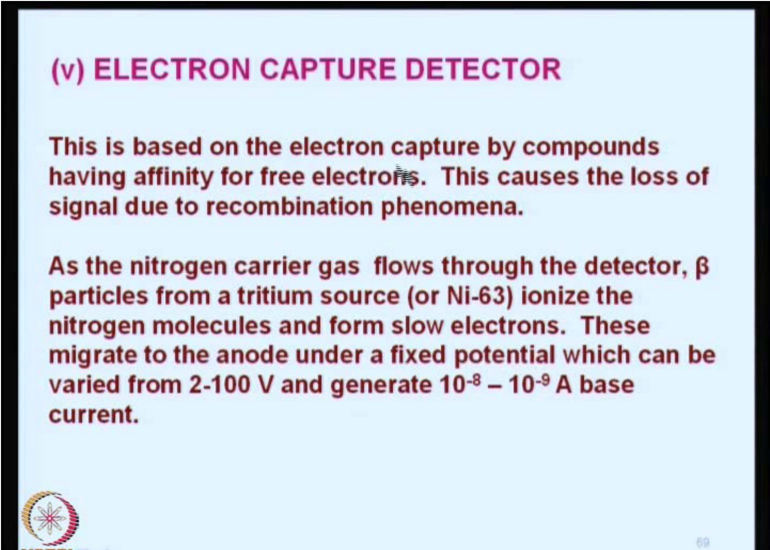
Now, we can discuss a little about phosphorous detector basically a phosphorous detector is a modified flame ionization detector only the difference is that the tip is being made of C C M bromide we just put a small coating of C C M bromide at the tip of the burner.

And then a compound containing phosphorous is burned alkali metals are released, because C C M bromide will decompose giving you C C M ions that is alkali metal ion and these alkali metals ionizes and increases the current flow; that means, we can

increase the sensitivity of the phosphorous substances by incorporating the C C M bromide which will increase the current and therefore, the detestability detection limit goes up to 10 raise to minus 12 grams.

And phosphorous compounds can be analyzed in this way, because most of the insecticides and pesticides and fertilizers especially in the storm water drains and in the plants metabolites all these are substances need to be analyzed only in this range about 10 raise to minus 12 grams. So, the unfortunately the LDR that is linear dynamic range for phosphorous detector is only about 1000 that is 10 raise to 3 compared to 10 raise to 6 of TCD, 10 raise to 7 of FID etcetera, but the detector is useful for the determination of phosphate additives in gasoline and pesticides also that is very important, because we do not have very simple methods for the separation of phosphate additives in gasoline and pesticides.

(Refer Slide Time: 22:28)



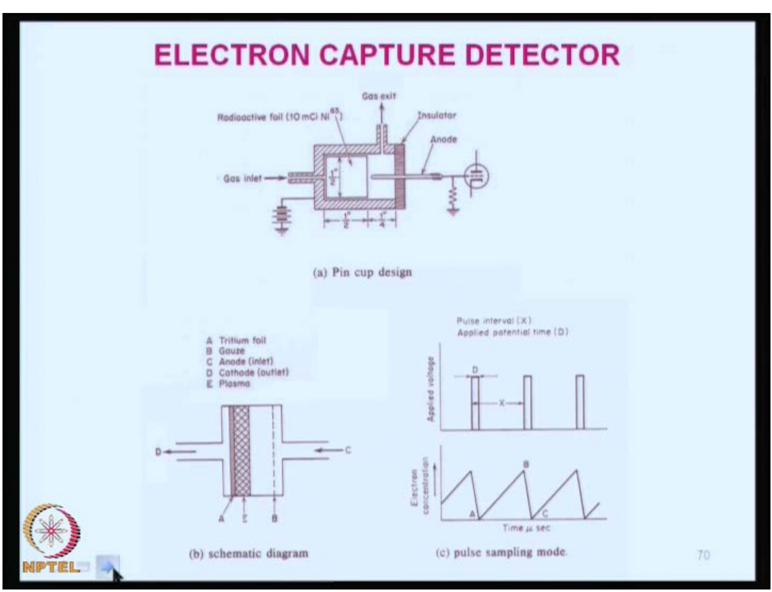
Now, I would like to discuss with you another kind of detector that is known as electron capture detector. This is based on the electron capture by compound having affinity for free electrons. Now, the idea is we have to generate free electrons and these free electrons need to be need to be attracted by the cathode and the during the process it causes the loss of signal due to recombination phenomena.

For example, as the nitrogen carrier gas flows through the detector the we are using the nickel 63 or a tritium source and we pass the carrier gas through the detector element that

is nickel 63 or tritium gas and beta particles from a tritium source ionize the nitrogen molecules that is carrier gas molecules are ionized and they form in turn slow electro, slow moving electrons are formed.

The slow moving electrons migrate to the anode under a fixed potential I can always fix a potential and try to attract them and the potential can be varied from 2 to 100 volts and generate a currents of about 10 raise to minus 8 to 10 raise to minus 9 amperes that is the base current.

(Refer Slide Time: 24:12)

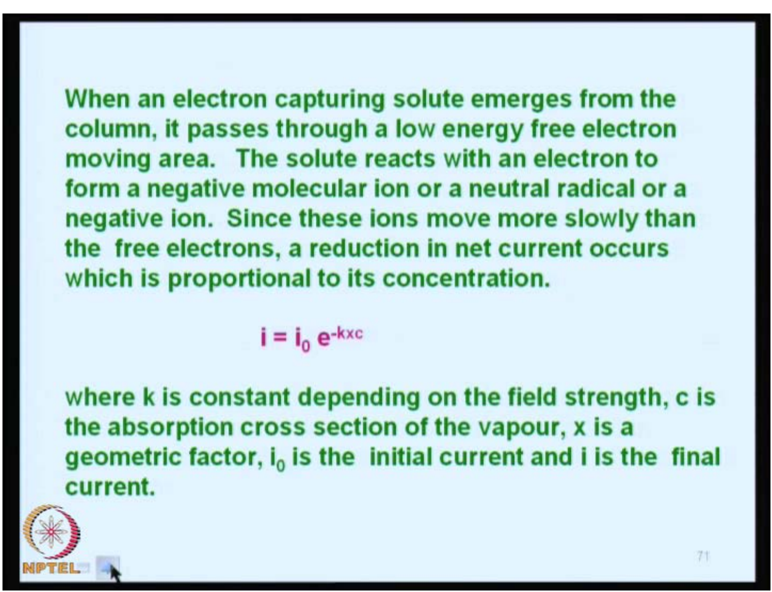


Now, you can this is the general arrangement of an electron capture detector you can see here, gas inlet is here and then I have a radioactive foil here and that is 10 mill curie of nickel 63 metal element and the whole size is about one-fourth and 1 half that is about three-fourth of an inch and the height is also about half an inch maximum the detector size itself is approximately about 1 inch or 1.5 inches.

So, the when the gas inlet is there here there is a detector and then grounding all other paraphernalia would be there and as the carrier gas comes in as the gas comes in, the electrons are captured by the components and reach the anode and the excess gas will flow out through this opening and the whole thing is insulated and this is known as pink cup design and here I have put a is tritium foil.

Here, the typical arrangement of this of this area is like this that is I have a here that is tritium foil B is a small gauze and C is the anode and D is the cathode that is the outlet and E is the plasma rain. So, this is a schematic diagram I can either have a pulse interval like this applied the signal would look like this. If, I have a pulse interval pick up or it can be in the pulse sampling mode I can do it like this and then collect the signal like this and in a reproducible manner.

(Refer Slide Time: 26:24)



So, this is the electronic capturing solution solute emerges from the column it will pass through a low energy free electron moving area, the solute will react with an electron to form a negative molecular ion. If, the solute reacts with an electron it will acquire negative energy. So, negative charge and then it can form either a negative molecular ion or a neutral radical or a negative ion.

Any of these three are possible since these ions move very slowly compared to free electrons free electrons do not have any mass. So, the free electrons would be moving much faster compared to these molecular ions or a neutral radical or a negative ion etcetera. So, reduction in the net current occurs which is proportional to its concentration it is a very simple way of putting the theoretical basis of the separation.

The current generated can be expressed in this form i is equal to i 0 into the e to the power of minus k x into c, where k is a constant depending upon the field strength and c is the absorption cross section of the vapour, x is a geometric factor i 0 is the initial

current and i is the final current. So, it is the reduction would be always less than i 0 and it can be quantified using this approximate equation.

Now, the E C D can be operated either in pulsed mode or a or under a constant voltage as I had shown you in the previous slide that is here, this is a constant and applied at pulse interval, I can measure that exact intervals or I can make it pulse sampling mode and the advantage is it is a pulsed current or a simple signal.

So, E C D is extremely sensitive to organic and inorganic halogen compound containing compounds, because halogen compounds have a an affinity for the electrons and they can form negative ions and all those possibilities are there similarly hydroxides can also capture the electrons, peroxides, yes. Conjugated carbon in compounds, yes. Similarly, nitrites nitrates ozone oxygen and organometallic compounds sulphur containing compound all these things can be separated and sensed using the electron capture detectors, but it is insensitive to hydrocarbons.

Because, hydrocarbons do not have the affinity to capture an electron and form a negative ion similarly amines they cannot be they do not have the affinity for the electrons, ketones same problem and pesticides and organometallic organometallics in gasoline they are the better candidates for the general application of such substances. Therefore, the E C D is only a specially required detector which you will have to specify when you buy gas chromatograph.

So, it is not that you should have all, the all types of the detectors that will depending upon the type of work you are planning you can go for TCD or FID or gas density detector or phosphorus detectors or electron capture detectors like that and then you will have to choose among these detectors whichever is most suitable for your applications.

And then by those things and then will be factory fitted onto the instrument whenever you buy the equipment. So, it is a very important concept of choosing a detector especially depending upon your work requirement.

In general, research institutions would go for TCD and FID that will suffice for most of their applications research institutes etcetera, but there are dedicated industries for example, pesticide industries and then environmental laboratories they would like to go

for FID, TCD and then electron captured detector depending upon the type of sample they want to separate and analyze.

(Refer Slide Time: 32:18)

(vi) OTHER DETECTORS

Flame emission, conductivity detectors, rf discharge detectors, infrared and mass spectrometer are other detectors.

RECORDING

The recorder should be generally 10 mv (full scale) fitted with a fast response pen (1 sec or less). The recorder should be connected with a series of good quality resistances connected across the input to attenuate the large signals. An integrator is a good addition too.

So, there are other detectors also. For example, there is a flame emission detector and then conductivity detector. If, the sample is able to conduct the electricity through the ions then we have conductivity detectors and we can have rf discharge detectors then I can simply connect an infrared spectrometer to the end of the column of a gas chromatography column and then I can all it g c i r and then g c m f s I can connect mass spectrometry to g c then I have a hyphenated technique known as g c m s.

Similarly, other detectors can be custom made provided you have that kind of applications in the mind, but I am not going into details of these detectors, because they are all driven by specific requirement of the chemical analysis and the type of sample what you would like to handle.

So, that completes our discussion on the detectors, but I would like to say that as another part of the instrumentation of gas chromatography it is important to have a recorder, the recorder should be generally of about 10 mill volts full scale fitted with a fast response pen. Nowadays, the response pen should be corresponding to should correspond to one second or less, but the recorder should be connected with a series of good quality resistances connected across the input to attenuate the large signal.

So, whenever you get a very large signal it must be attenuated and then it should be recorded and you can add an integrator to determine the total area of a signal that is also a must. Nowadays, what is happening is most of the signals are recorded in the computer and you can take a print out.

And the computer recording is much simpler; because most of these things are already incorporated features can already be incorporated in including the peak area measurement integration and then quantity quantization followed by the estimation and statistical evaluation. All those things are possible if you are able to connect it to a computer. So, again in most of the modern instruments microprocessor is a form a microprocessor forms a very important component in almost all these equipments and recording is no exception.

(Refer Slide Time: 35:28)

So, the the other part of the gas chromatography gas chromatography equipment is the thermal compartment that is the big box that what I would I would say that, the whole the whole gas chromatographic equipment should be put in a big box and the everything has to be controlled precisely to plus or minus 0.1 degree centigrade and that is a the column should be controlled, injection block should be controlled, column oven should be controlled and then detection detector units must be controlled and all these things must be controlled up to 0.1 degree centigrade accuracy.

Maximum operating temperature for example, in gas chromatography also is a very important concept, because many of the organic substances what you are using for coating the column they will start decomposing. So, there is always a limit to which your gas chromatographic analysis can be taken that far. So, that temperature is about 500 degree centigrade.

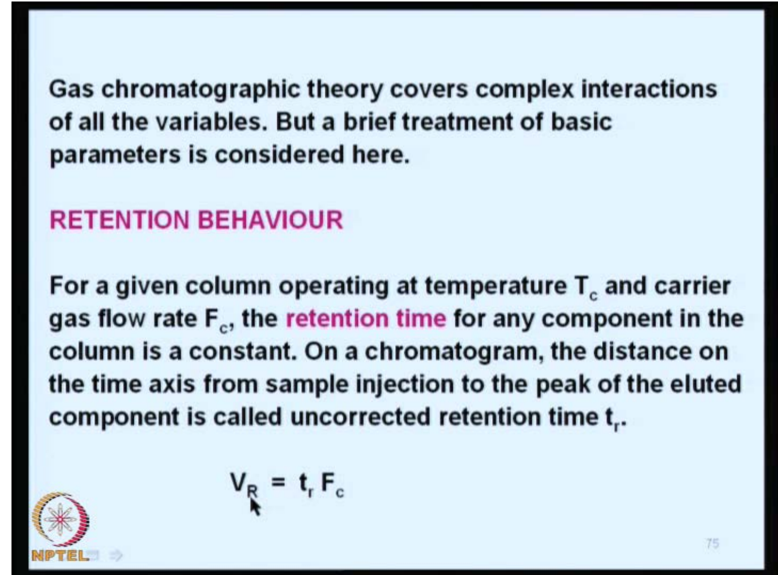
So, therefore, separate heater for each the column injection block and column oven and detector, etcetera they they need separate heaters for maintaining the temperature and also to have a rapid heating protocols.

So, that is a must therefore, sometimes what happens is the moment you take out a sample again you one everything is heated you cannot inject another sample. So, you need to cool the whole system. So, rapid cooling is also essential for multiple operations. So, that is the function of the thermal compartment.

Now, let us discuss a little about the gas chromatographic theory, because it is generally we have discussed this in the initial stages, but with respect to gas chromatography we have not discussed and the gas chromatographic theory actually covers complex interactions of all the variables, but a brief treatment of the basic parameters we can consider and one of them is retention behavior.

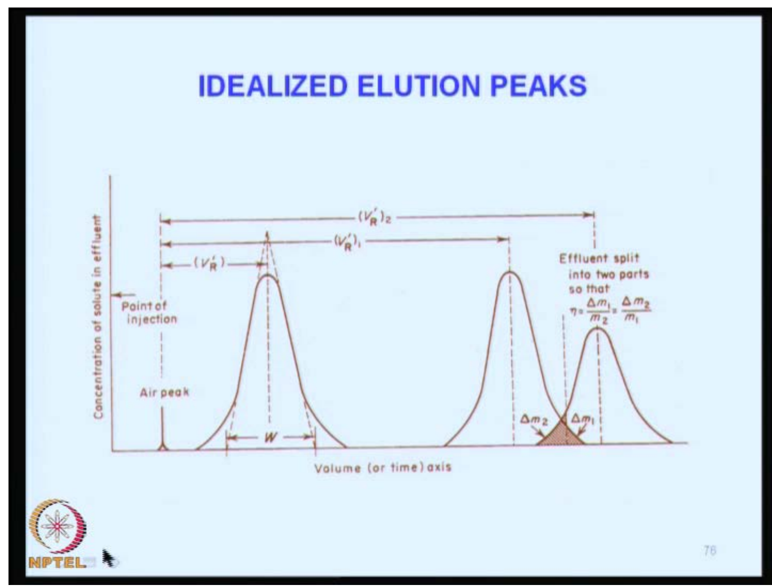
The retention behavior is again a function of the carrier gas flow rate and the operating temperature; the retention time also can be for any component for a given column is a constant. So, on the chromatogram the distance on the time axis from the sample injection to the peak of the eluted component is called uncorrected retention time you would see most of it as the you will see a small air signal whenever you see a gas chromatograph and from there you can calculate the retention times.

(Refer Slide Time: 38:45)



Now, this slide will show you that the retention time is defined by V R that is a function of t r and F c, F c is the gas flow rate and t r is the retention time now these are the ionized, idealized elution peaks. Here, you can see that this is an air peak and this is V R dash and this is where the peak is coming and this is the V R another for another component third component etcetera and effluent is usually split into two parts.

(Refer Slide Time: 39:04)



So, that delta m 1 bar delta m 2 and delta m 2 bar delta m 1 should be equal because in this case there is some amount of mixing of the 2 peaks. So, this kind of separation is not

very ideal. So, ideal would be like this part. So, this is the volume or time axis and this is the concentration of solute in the effluent that is the y axis.

(Refer Slide Time: 39:58)

Gas flow rate must be corrected to the column temperature and outlet temperature P. The air spike measures the transit time for a non retained substance. Converted to volume V_m, it represents the interstitial volume of the gaseous phase in the column plus the effective volume contribution of the injector port and detection. Thus V^I_R has to be corrected for dead space.

$$V^I_R = t_r F_c - t_{air} F_c = V_R - V_M$$

Since gas moves more slowly near the inlet than at the exit of the column, a pressure gradient correction or a compressibility factor j to V^I_R must be applied to get the net retention volume.

Now, gas flow rate must be corrected to the column temperature and outlet temperature P it is very important, because we are we have to remember that we are dealing with the dealing with the gas.

So, the temperature also must be related to the pressure. So, temperature and pressure must be co related the air spike usually measures the transit time for a non-retained substance. So, converted to volume V M it represents basically the interstitial volume of the gaseous phase in the column plus the effective volume contribution of the injector port and detection detector detection unit or detector whatever it is.

Here, I have written detection. So, the v therefore, V R dash and that has to be corrected for the dead space how do we do that that is t r into F c minus t air into F c. So, in general; that means, we are basically correcting the volume. So, we can represent it as V R minus V M.

Since the usually the gas moves more slowly near the inlet than at the exit column this is a very standard observation. So, pressure gradient correction or a compressibility factor j must be applied to V R dash that is to this volume to get the net retention volume.

(Refer Slide Time: 41:30)

$V_N = j V'_R$ where $J = \frac{3}{2} \frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]}$

Since $V_R C_M = V_M C_M + V_S C_S$

$V_R = V_M + K_d V_S$

or $K_d V_S = V_R - V_M = K_d (w_L/\rho_L)$

where w_L = weight of liquid phase,
ρ_L = density of liquid phase

$V_g = (273/\rho_L)(K_d/T_C)$ = specific retention volume

where or $K_d = V_g \cdot \rho_L (T_C/273)$ or $V_g = (273/\rho_L)(K_d/T_C)$

So, we write V N is equal to that is a net retention volume; V N is given by a compressibility factor multiplied by V R dash, where J is given by this number 3 by 2 into P I by P 0 whole square divided minus 1 divided by P 0 whole to 3 minus 1.

Now, you can see that we are into C M is equal to V M into C M plus V S into C S this we have discussed in the first class in the first class in of the chromatographic separations.

So, you can write V R is equal to V M into V M plus K d into V S, where V incorporates the partition coefficient. Now, we can also write K d into V S is equal to V R minus V M in that should be equal to K d into W L divided by rho L and the W L actually represents the weight of the liquid phase and rho L is the density of the liquid phase.

We can calculate V g that is specific retention volume for any substance and that is given by 273 rho one. Now, we are we are in involved in the density of the substance and multiplied by K d by T C, where K d is given by this expression. So, we can actually calculate the actual the separation retention volume based on the density as well as partition coefficient as related to T C.

(Refer Slide Time: 43:14)

TEMPERATURE DEPENDENCE

$$\log V_g = \frac{\Delta H}{2.3\,RT_C} + \text{const}$$

ΔH = partial molar heat of the solute in the liquid phase

By plotting, $\log V_g \rho_L$ Vs $1/T_C$, $\Delta H / 2.3\,R$ may be obtained which is a linear function.

Lower operating temperature leads to increased retention. Every 30^0 C reduction will double the retention volume.

So, the temperature dependence is again a very important concept, because I would like to say that it has something to do with the enthalpy. So, the enthalpy can be related to V g that is according to this expression if you write in the slide log V g is given by enthalpy divided by 2.3 R into T C plus it is some constant rho of incorporate.

And where in this equation delta H is the partial molar heat of the solute in the liquid phase. So, we can plot log V g into rho L versus 1 over T C, if you plot log V g versus 1 over T C, the remaining part delta H upon 2.3 R is obtained as a slope of the equation and which is should be a linear function.

Therefore, lower operating temperature normally leads to increase the retention time you reduce the temperature you reduce the temperature the substances will be held in the column for longer time.

So, is there a benchmark, the benchmark is every 30 degree centigrade reduction will double the retention time approximately not exactly for all compounds, but in general whenever we run a gas chromatograph you are interested in retaining the column, because support material if you remember when we discuss the columns they all contains liquid substances coated onto solid inorganic supports like diatomaceous, earth silver etcetera.

If you operate it at higher temperature then what happens many of the substances that are coated will also evaporate and the concentration of the liquid phase that is stationary phase will come down therefore, it is always preferable to operate a gas chromatograph at as low temperature as possible.

But, how much low? So, the depending upon the importance of the component importance of the liquid phase and importance of the of the speed of analysis you should always work out, whether you would like to have a longer retention time or shorter retention time.

And if you want to have a longer retention time approximate idea can be obtained by reducing the retention time, that is reducing the temperature by about 30 degree will double the reaction time.

(Refer Slide Time: 46:46)

A knowledge of ΔH and V_g helps in calculating the order in which peaks will emerge.

e.g > 67^0 C methyl cyclopentane and 2,4 dimethyl pentane

< 67^0 C 2,4 dimethyl cyclopentanone and methyl cyclopentane

80

So, knowledge of enthalpy and V g, in general it helps in calculating the order in which the peaks will emerge for example, below 67 degree centigrade if I take a look at the enthalpy in V g of these 2 substances methyl cyclopentane will come out first and 2, 4 dimethyl pentane will come out next.

Now, higher than 67 degree centigrade if I maintain the column temperature, what I get is, the order will get reversed that is 2 4 dimethyl cyclopentane will come first and methyl cyclopentane will come later that is also possible.

Now, I would like to say a few words about the relative retention time the relative retention time is expressed as a the ratio of the retention time with respect to a standard, because whenever we want to separate any compound of unknown character, you should always do separation with a known substance whose retention time is known. So, that we can standardize all parameters with respect to the known standard and then you can try to the unknown separations.

(Refer Slide Time: 48:16)

RELATIVE RETENTION

Expressed as ratio of the retention time of a standard.

$\alpha = t'_R / t'_R \text{ std} = (K_d)_2 / (K_d)_1$

α is independent of column length, carrier flow rate, compressibility factor , liquid solid support ratio etc.

Retentions for various solute classes are tabulated for typical stationary phases which helps in estimating whether a mixture can be separated or not. Such tabulations will be found in the J.chrom, science, journal of gas chromatography, chromatography reviews, texts etc.

So, I would like to write an expression something like this that is alpha is equal to t R dash divided by t R dash multiplied by the standard, t R dash of the standard material that can be written as K d 2 divided by K d 1, because all other all other times will vanish, because if I have only the sample in standard there will be only these two terms will remain.

So, alpha is basically independent of the column length and then it is independent of the carrier gas flow rate it is independent of the compressibility factor and liquid solid support ratio etcetera. So, especially when you want to express relative retentions then you should go for this kind of ratios.

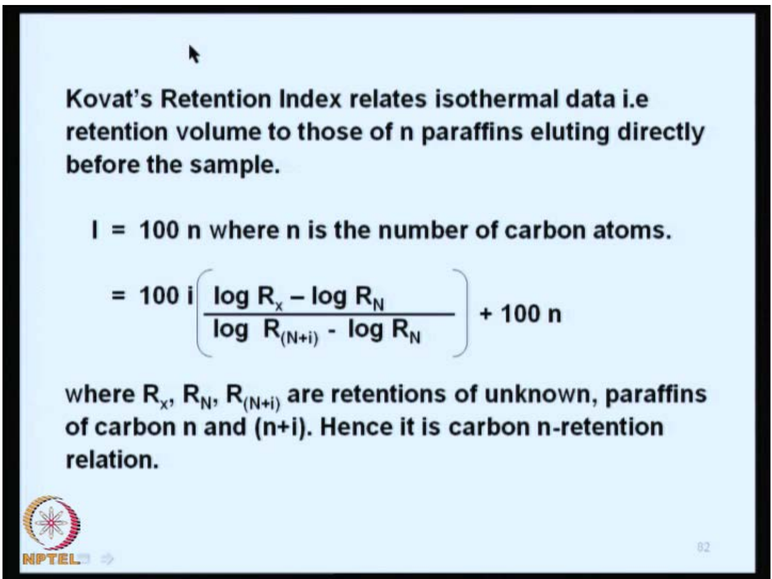
So, I can have retentions for various solute classes tabulated for typical stationary phases for a given stationary phase I can pass through number of number of substances belonging to the same category. For example, methane, pentane, butane, hexane, nonane all such substances belong to a class that is known as hydrocarbons.

And these hydrocarbons if I pass through a known column a single column and then try to compare then I can have a database of how the samples will behave. So, retention times for various solute classes like this alcohols, hydrocarbons, ketones, aldihydes etcetera they are tabulated for typical stationary phases which helps in estimating whether a mixture can be separated or not. If, I know the relative retention time for each compound.

So, if I have a suspicion of the compounds, what I have in my sample all I have to do is take a look at the relative standard retention times and form a plan how I can separate my mixture. So, the tabulate at the typical stationary phases in general help in the estimating whether a mixture can be separated or not in the first place and then if it can be separated how do we go about? Doing the separation.

So, such tabulations are usually found in journal of chromatographic science journal of gas chromatography several other chromatographic their dedicated journals for chromatography are there. Then there is chromatography review also is there and then several text books on gas chromatography they also give you lot of information with respect to these substances that is the relative retention times.

(Refer Slide Time: 51:28)

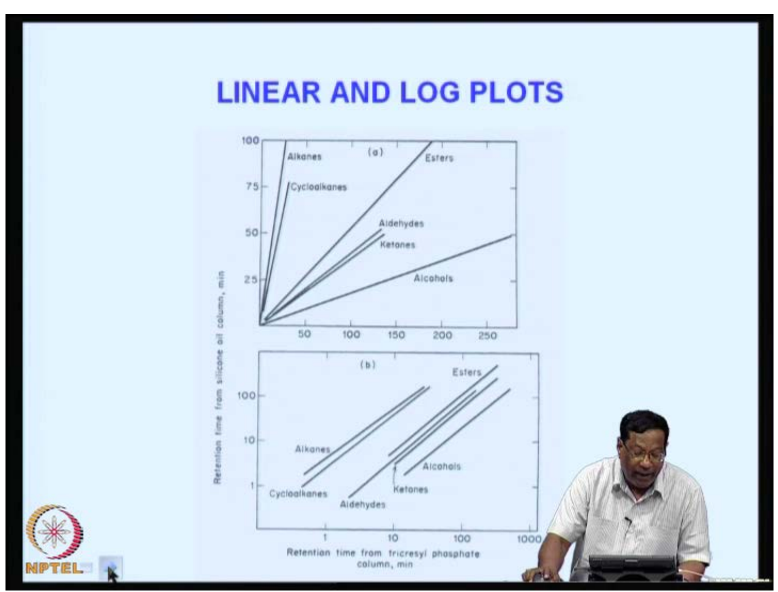


Now, there is something known as kovat's retention index. Now, this kovat's retention index basically it relates the isothermal data that is retention volume to those of n

paraffins; that is paraffins containing n number of carbon atoms that is different carbon atoms eluting directly before the sample.

So, the index is given by 100 into n where n is the number of carbon atoms in a given sample. So, expanded the R X k that is 100 I into log R X minus log R N this thing etcetera index is R x, R N and R N plus 1 are the retentions of unknowns paraffins of carbon atoms, n carbons paraffins containing n number of carbon atoms and paraffins containing n plus i number of carbon atom. Therefore it is a carbon n retention relationship; that means, number of carbons relation retention times based on these things.

(Refer Slide Time: 52:45)



So, we can have some sort of a plot like this based on the retention index, we can see here all these are the numbers which are retention times from triglyceride phosphate column, this is for alcohols, this is for ketones this is for aldehydes, esters, cycloalkanes, alkanes. And then here at the bottom I have listed alcohols, ketones, aldehydes, esters, cycloalkanes and alkanes etcetera. And these having these figures will help me in analyzing a random substance from from a given mixture.

(Refer Slide Time: 53:25)

APPLICATIONS OF GAS CHROMATOGRAPHY

1. Reaction gas chromatography

The injected substances pass through a reaction zone ahead or within the injection port or in a column or post column.

So, if I know the coherts retention index I will know what should be the temperature how long it will be held, what should be my column temperature, oven temperature and other things because there there are several data available based on coherts retention index what would be the optimum parameters further separation from a given mixture.

Now, what are the let us discuss a little about the applications of gas chromatography. So far, we have discussed about the instrumentation and then theoretical basis, but the average discussion on gas chromatography will never be complete without the applications.

Because, the applications are as varied as numerous, as the gas chromatograph they actually there are millions of gas chromatograms all over the world and daily millions of compounds are being analyzed by gas chromatography.

So, it is a very very important component in any analytical science laboratory. So, there is something known as the optimum utilization of a given instrument. So, if you are the substance is given to you in a readymade form readymade mixture and you know how to separate job is done and well and good.

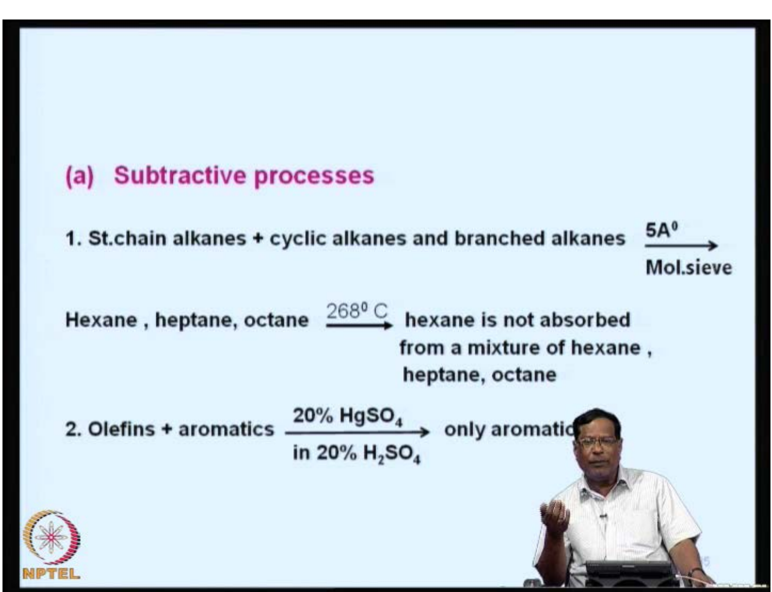
But, there are sometimes situations where you would like to separate the components not only on the role as they emerge from the column, but also we would like to tinker with the chemical properties of the substances which you want to separate.

Now, these things such reactions for small editions which you can small tricks you can say that, small tricks which you can handle in a gas chromatography are the things which make gas chromatography. So, much versatile in the end.

Therefore, let us I want to talk to you about reaction gas chromatography, actually in reaction gas chromatography the injected substances pass through a small reaction zone ahead of the column or within the injection port or inside a column or post column also.

Basically, the idea is to pass the sample through a zone in which some certain reactions are ensured and the products are coming over different products are coming out which can be sensed depending upon the requirement.

(Refer Slide Time: 56:36)



Now, you can see that there are different kinds of reactions one can carry out inside a gas chromatograph. For example, this is subtractive process if you have straight chain alkanes and then cyclic alkanes and branched alkanes all the three are we are having a mixture and we like to separate them.

The best thing is to have a column of molecular sieve of for a angstrom molecular sieve then all these things can be separated. I have one example of hexane heptane and octane which is to be separated around 268 degree centigrade.

And then hexane is not absorbed from a mixture of hexane heptane and octane. So, only hexane will come out if you carry out the separation using this now imagines that you have a mixture of olefins and aromatics.

Olefins are ethylenic compound and aromatics are aromatic compounds and you know more about it. So, if this they can be separated pass through a column containing 20 percent mercuric sulphate, in 20 percent of hydro sulphuric acid through small reaction zone only aromatics will come out olefins will get absorbed they will not come out.

So, your separation is achieved you can quantitatively estimate and many other things can be done once you can pass it through the solution once without solution. You can estimate both similar things or tricks we employ in gas chromatography. We will continue our discussions in the next class.