Modern Instrumental Methods of Analysis

Prof. J. R. Mudakavi

Department of chemical engineering

The Indian institute of science, Bangalore

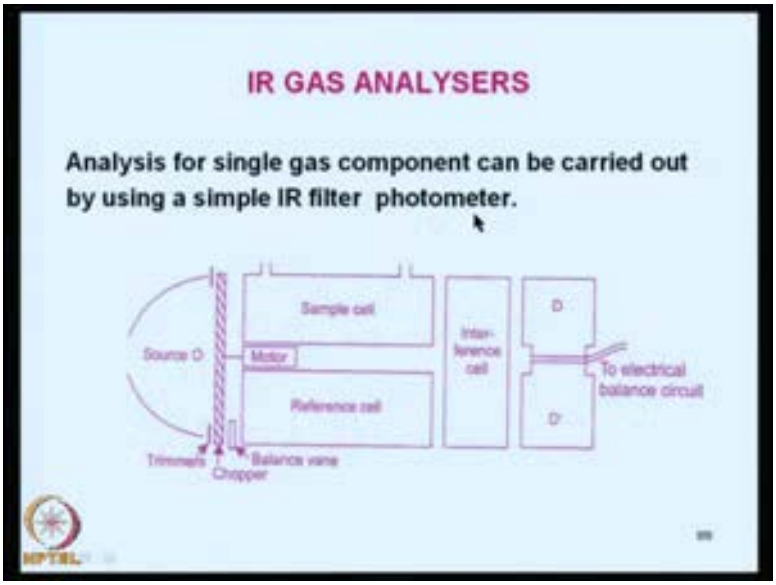
Lecture No. # 33

Infrared Spectroscopy- 3

Non-dispensive IR, Mass spectrometry

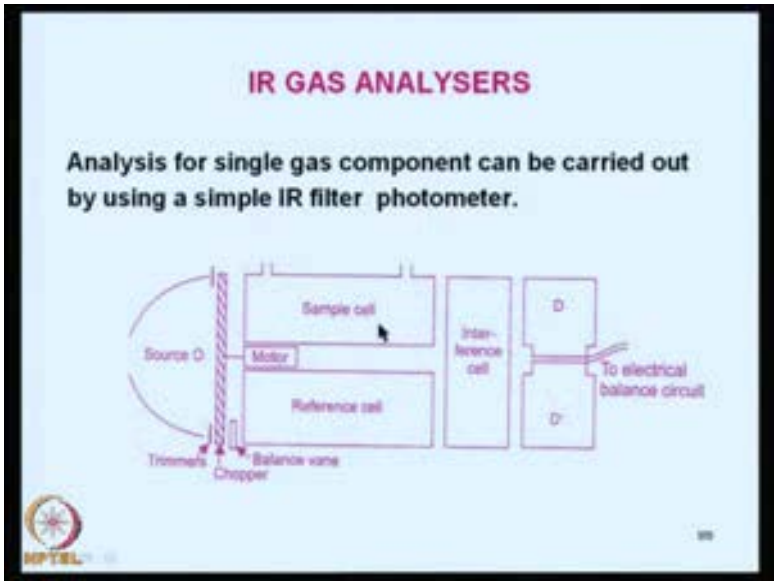
In the last class, we have discussed about the infrared gas analyzers and these are essentially infrared filter photometers; that means no monochromator is required for the analysis of process gases.

(Refer Slide Time: 00:31)



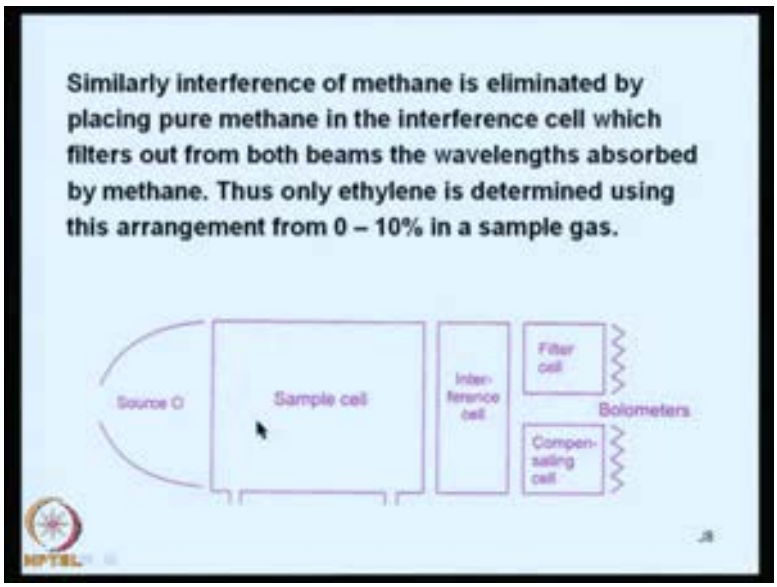
So, I wanted you to remember that the infrared radiation is split into two beams and then directed towards bolo meters wired in a balance circuit. The sample gas flows through one cell and the reference gas flows through another cell. And there is a separate detector for each sample gas as well as the reference gas connected to two bolo meters, which are interconnected again with by means of a diaphragm.

(Refer Slide Time: 00:31)



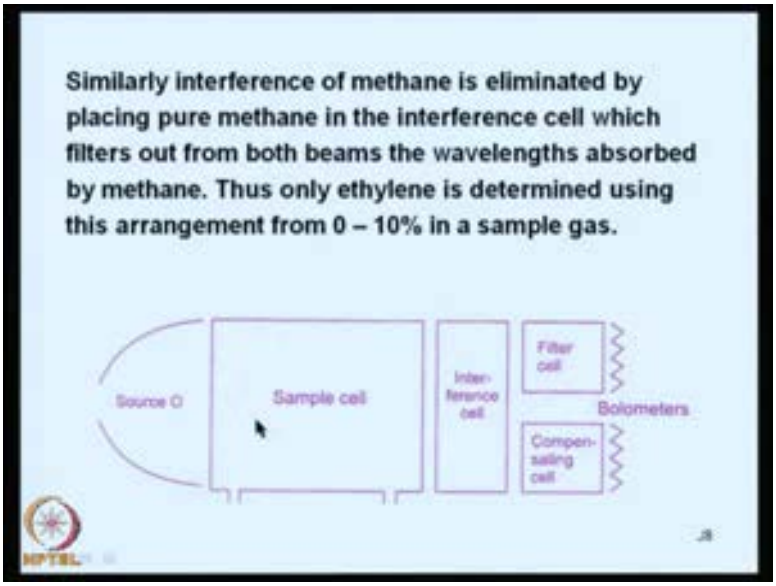
This figure I had shown you there is a sample cell and a reference cell. This is an interference cell and these two are bolo meters separated by an electrical balancing unit. And in the interference cell, you can put any of the other process gases which may interfere in the analysis. So, when the sample cell contains the analyte, the only the analyte will be absorbing the radiation and this diaphragm will be pushed down stairs and which is balanced electrically to give you a reading of the electrical signal, which is again correlated to the concentration of the analysis, concentration of the analyte gas. Now, this is one arrangement.

(Refer Slide Time: 02:10)



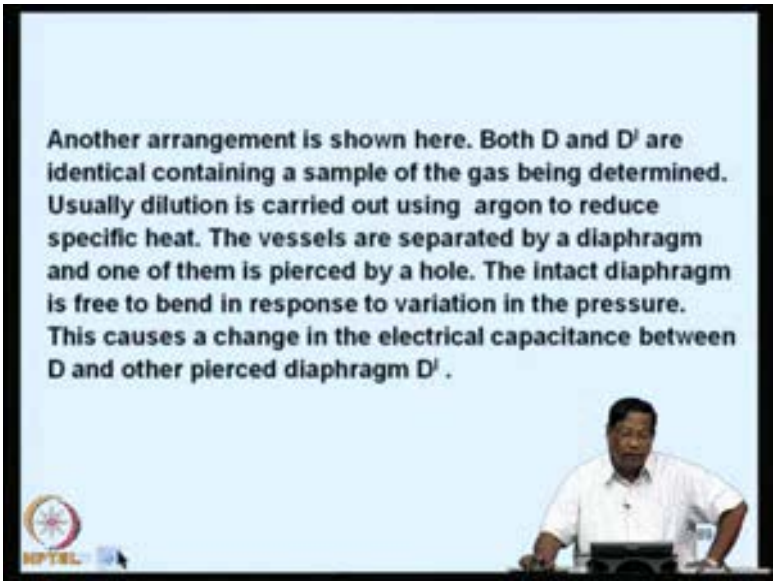
Another arrangement is like this that you have a simple same sample cell; there are no reference cell here, but you have an interference cell, and again, you have a filter cell and a compensating cell. So, as the radiation from the source is directed towards the sample cell, the absorbance will take place and interference cell will absorb all the other radiations except the analyte. So, the radiation from the analyte is going to fall on to the bolo meters and the filter cell and compensating cell will work in tandem to give you the signal.

(Refer Slide Time: 02:10)



So, the interference of methane, for example, can be eliminated by putting pure methane in the interference cell here here and which filters out from both beams the wavelength absorbed by methane. Thus only ethylene is determined using his arrangement from 0 to 10 percent in a sample gas. So, such arrangements are useful for the determination of process gases and number of, number of, process gases can be analyzed.

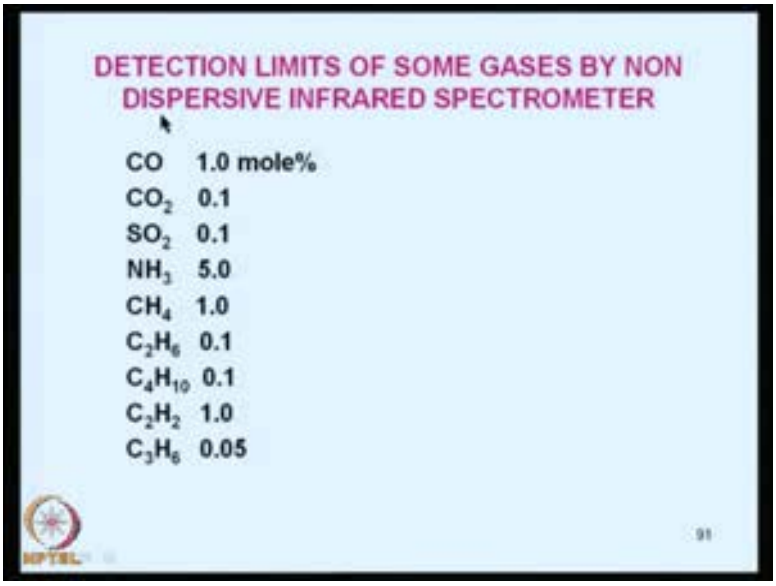
(Refer Slide Time: 03:24)



And the only arrangement you have to remember is that both d and d dash in the previous signal in the previous arrangement here d and d dash are identical containing a sample of the gas being determined. Usually, dilution is required and this dilution is accomplished using argon and the dilution is require to reduce the specific heat of the gas. The vessels are usually as usual separated by a diaphragm and one of them appears by a hole. And the intact diaphragm is free to bend in response to the variation in the pressure and this causes a change in the electrical capacitance between d and d dash which will result in an electrical signal.

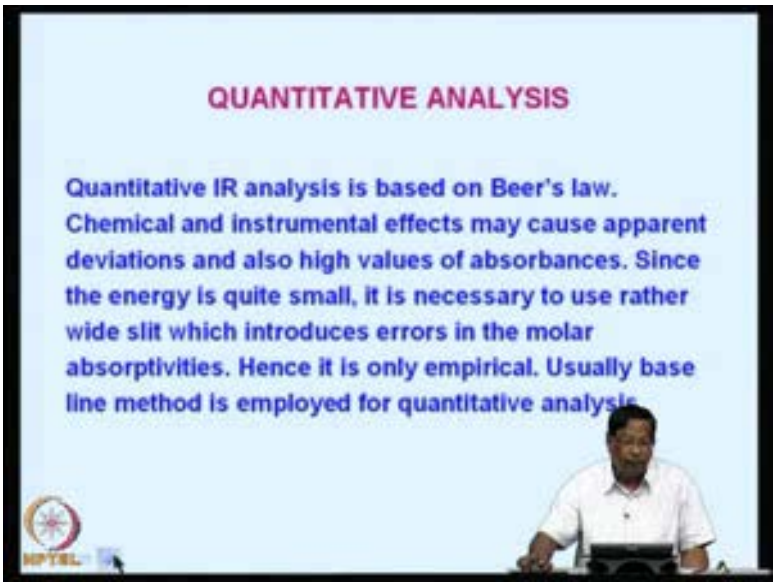
So, you can, the difference in pressure depends again on the temperature, which is in turn dependent upon the infrared radiation absorbed. The reference cell is filled with dry nitrogen and sealed off; you do not have to deal with that again once you buy the equipment. And the two diaphragms constitute a capacitor which I had already told you, which is incorporated in a high frequency electronic circuit, which eventually energizes a small motor to drive a balancing wing across the reference beam till they match.

(Refer Slide Time: 05:27)



So, the difference of this moment is, is, recorded as a signal; that is a very simple arrangement and detection limits of some of the gases determine by this technique. I am showing you here, for example, CO is 1.0%,1.0 mole % and CO2 is .1, SO2 is .1, NH2 is .5 like that. This is methane; next is ethane, butane, acetylene and c three h six, etcetera.

(Refer Slide Time: 05:52)



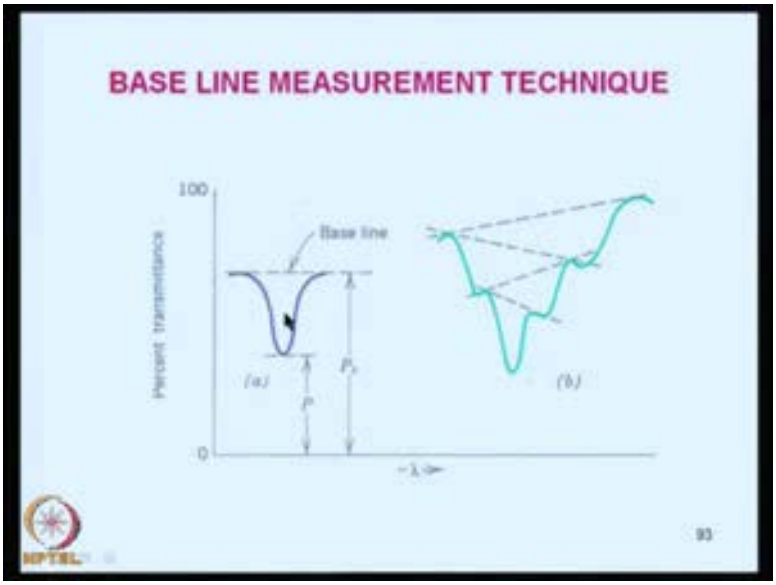
So, the chemical analysis of process gases can be done like this using the non-dispersive infrared. The same instruments can also be used for the determination of carbon-dioxide that is non-dispersive infrared spectrometer spectrometry even in ambient temperatures,

that is, in the pollution control studies etcetera; one can determine the concentration of carbon dioxide in the air and carbon monoxide in the air nitrogen oxides, etcetera. They can also be determined using non-dispersive infrared spectrometry

Now, that is, that apart. We should discuss how quantitative analysis is being performed using infrared spectrometry. As I told you earlier the quantitative analysis is based on the Beer-Lambert's law; that means, chemical and instrumental methods effects may cause apparent deviations and also high values of absorbance. Since the energy is quite small, it is necessary to use rather wider slits which introduces again errors in the molar absorptivities.

Therefore, it is the Beer-Lambert's law concentration relation with respect to IR absorption is, is, only limited to empirical values rather than exact concentration determinations. Usually, a base line method is employed for quantitative analysis.

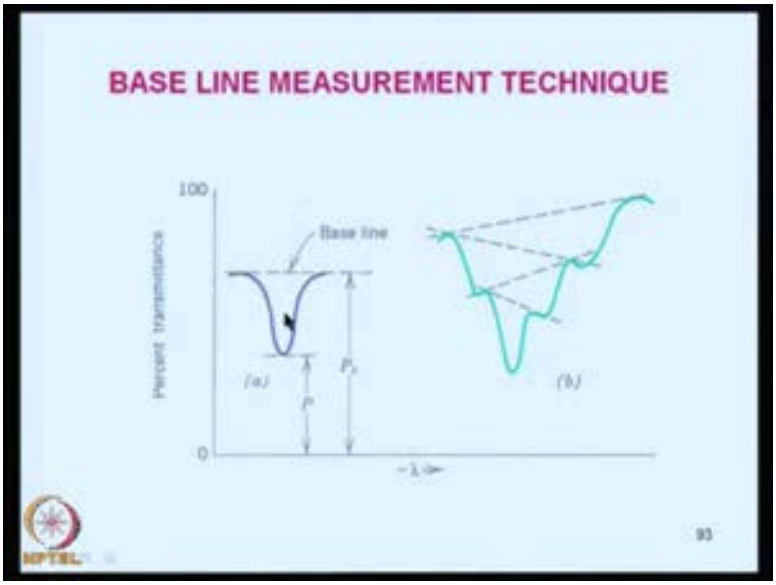
(Refer Slide Time: 07:43)



So, here, I am showing you how IR peak looks like this looks, and here, this is the percent transmittance versus wavelength and the concentration of the substance is known by weighing, and suppose this is an IR peak - infrared peak - and the total transmittance is this much p 0 and this is p, the difference is absorbed and you have to draw a base line along the tangent and you can measure the peak area and determine the concentration.

So, if you have different concentrations of the substances, then it is possible to prepare a calibration curve corresponding to different concentration and then plot peak area or absorbance whichever is convenient and you can determine the quantitatively the amount of the sample present in a given system.

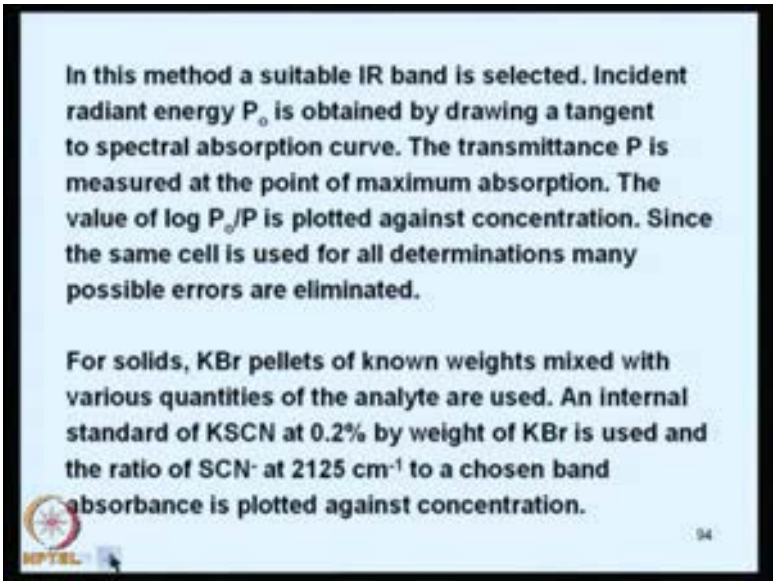
(Refer Slide Time: 07:43)



So, the slide also shows a complicated infrared range here. In the first case, the tangent is very easy to draw. Here, in the second case, in this region, you can see that there are a number of peaks - one is here; another is here; another is here like that so many tangents are possible, but all these things can be incorporated to obtain different kinds of absorbances, different kinds of different values of absorbances and then the concentration can be determined.

.

(Refer Slide Time: 09:07)



Basically a suitable IR band must be selected which is responsive to the functional group present in the sample. So, incident energy p naught is obtained by drawing a tangent to spectral absorption curve. This is the tangent what we had discussed earlier. And the transmittance is measured at the point of maximum absorption. The value of log of p naught by p is plotted against concentration. Since the same cell is used for all determinations many possible errors are automatically eliminated.

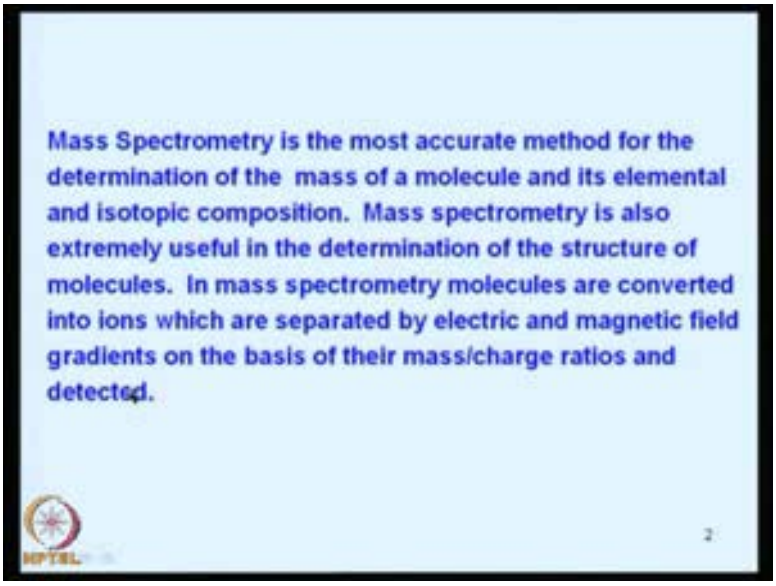
Now, what do you do for solids? So, in solids, potassium bromide plates of known weights are mixed with the various quantities of the analyte and you can take a internal standard of potassium thiocyanate or something like that by 0.2 percent by weight of the k v r and the ratio of thiocyanate at 2125 centimeters. That is the standard frequency of the IR absorbance for thiocyanate - 2125 centimeters inverse. The ratio of the actual peak corresponding to thiocyanate peak is chosen and it is plotted against the concentration.

(Refer Slide Time: 11:06)

This is a typical infrared spectrum IR instrument, you are, it looks like a nice box, but you can see that the left side would be the source here and this is sample compartment which opens up and this is the optics and the computer controlled instrument; such instruments are readily available in the market. So, I would like to show you that typical infrared analysis can be performed using the techniques what I have taught you so far.

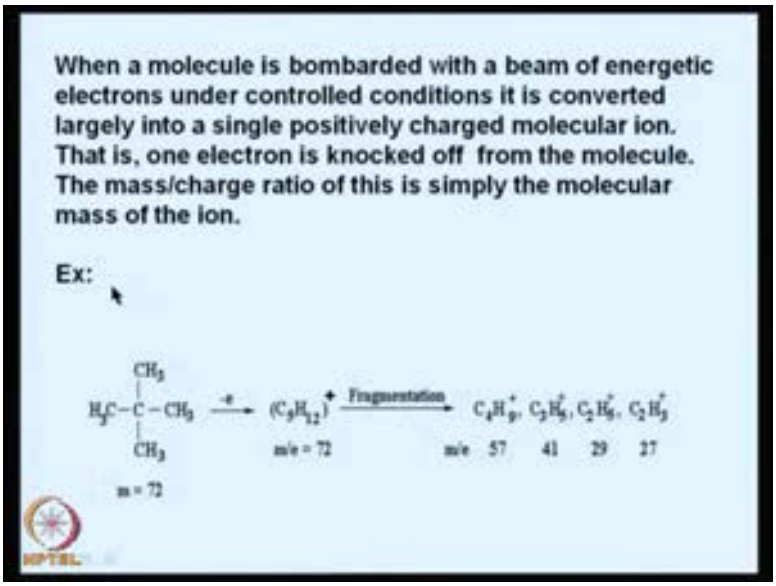
Now, I will stop here discussing about the infrared, but I will take you to another technique, that is, mass spectrometry. Now, this is another technique that is usually that is useful for the chemical analysis of substances mostly limited to organic, but inorganic mass spectrometry also can be conducted as and when required; that means, the whole analysis is based on the mass determination of the ions. So,

(Refer Slide Time: 12:53)



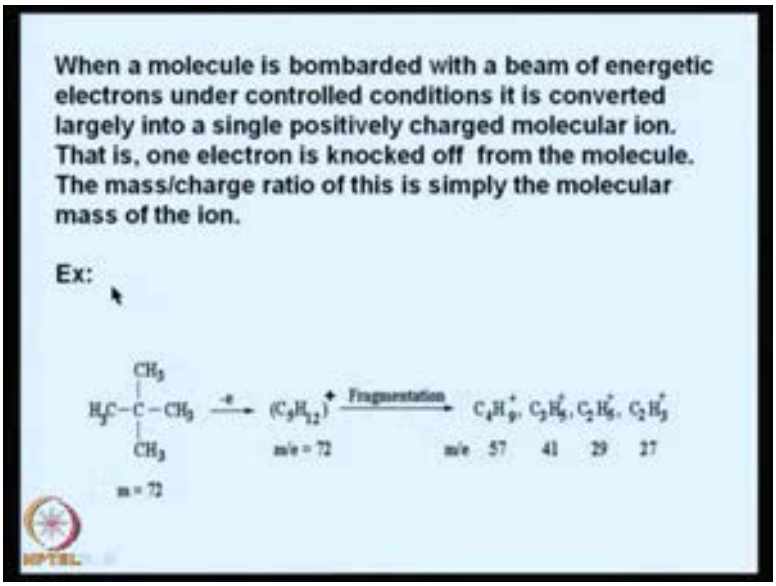
The mass spectrometry is basically a technique most accurate for the determination of the mass of a molecule and its elemental and elemental and isotopic compositions. Mass spectrometry is also extremely useful in the determination of the structure of the molecules, and in mass spectrometry, molecules are usually converted into ions which are separated by electric and magnetic field gradients on the basis of their mass to charge ratio and this mass to charge ratio are detected using the mass spectrometry.

(Refer Slide Time: 13:39)



So, when a molecule is bombarded with a beam of energetic electrons, you take a molecule bombard it with a beam of energetic electrons under controlled conditions it is converted largely into single positively charged molecular ion; that means, one electron is knocked off from the molecule and the mass does not change, because the mass of an electron is about 1 by 1645 times less than that of a proton. So, the loss of an electron does not result in any substantial change in the mass of the molecule and because it is an ion owing to the loss of an electron; we call it molecular ion only when an electron lost from the whole molecule, that is, one electron is knocked off from the molecule and the mass to charge ratio of this is simply the molecular mass of the ion.

(Refer Slide Time: 13:39)

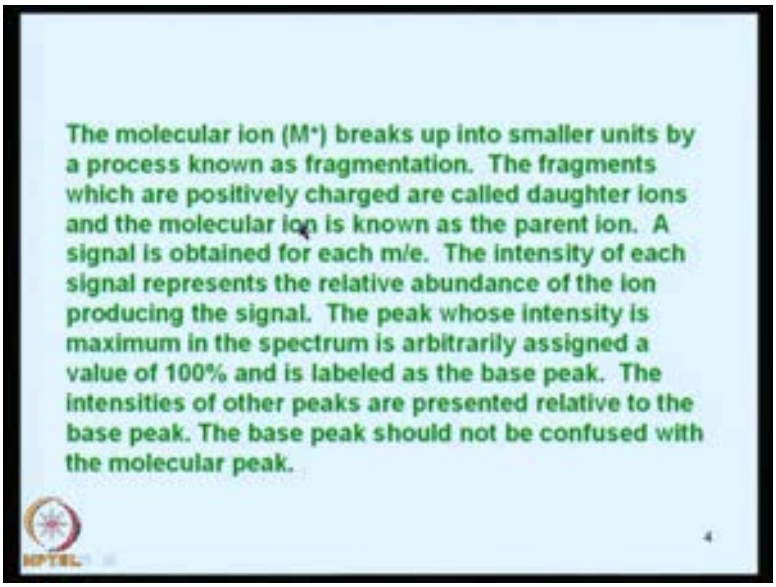


For example take a look at this equation. We have this compound tetra methane butane; this is 1, 2, 3, 2 2 dash dimethyle propane and if you knock off the molecular weight is 72, that is, carbon there are 1, 2, 3, 4, 5 carbon atoms. There is 60 and twelve hydrogen atoms that is 6 12. So, the total mass of the this molecule is 72

If we knock off one electron from here, what we get is a molecular ion, that is, with the same molecular weight, but carrying a positive charge and this molecule may further undergo decomposition to produce other mass ions. For example, the, this is C4H9 plus is possible with a 57mass by e ratio. Then we have C3H5 plus with 41; C2H5plus is 29; C2H3e plus is 27 something like that a number of other ions produce by the fragmentation of the molecular ion are produced and because their masses are also

differing 57,41,29,27 etcetera, they are also detectable along with the molecular mass, that is, 72 peak.

(Refer Slide Time: 16:25)



So, the molecular ion breaks up into smaller units by a process known as fragmentation. The fragments which are positively charged are called as daughter ions and the molecular ion is known as the parent ion. So, a signal is obtained for each m by e ratio. The intensity of each signal depends again upon the relative concentration rather abundance of the each ion producing the signal.

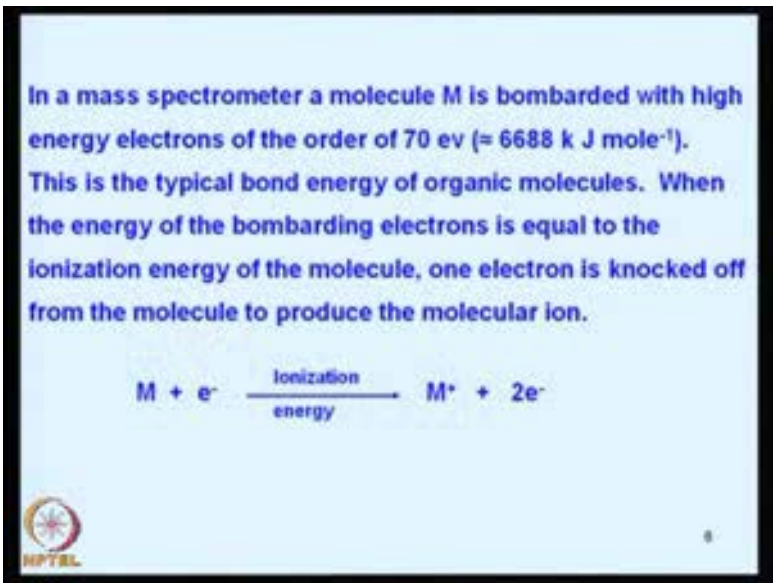
So, the peak whose intensity is maximum in the spectrum is arbitrarily assigned a value of 100 and all other peaks are calculated corresponding to this ion, that is, maximum abundant ion and the 100 percent peak is known as base peak. The intensities of other peaks are presented relative to the base peak. So, the base peak should not be confused with the molecular peaks.

Sometimes molecular peaks may be most intense but it is not the case all the time. So, one has to be a little careful when you are looking at the mass spectrometry, mass spectrum of a compound because molecular ion is the one which is showing you the highest molecular weight; that is the parent ion. All others would be this thing, but the molecular ion need not be hundred percent base peak.

So, the mass spectrum is essentially a graphic plot of the intensity versus m by e ratio. So, no two compounds can have an exactly similar mass spectrum that is understood because with each compa edition of an element even including hydrogen, that is, it will add a mass of one unit. So, the mass spectrum of a compound can be used as a finger print of a molecule. Any molecule if you want to know, what is the, what is the compound? First choice is go for a mass spectrum. So, find out what is the molecular weight and that molecular ion and molecular weight and then you can determine the different kind of structures that are possible by knowing the elemental composition also. So, very small amounts of samples are required for the mass spectrometric analysis

And mixtures can be analyzed easily, but the spectrum m by e mass spectrum would become complicated because mixtures means there are several other compounds, in which, you may be or may not be interested and you have to discount the other molecular ions, if the, if you know there are mixtures. It is also useful also for unraveling the reaction mechanisms of the organic compounds and the identification of functional groups is quite possible in organic compounds. It is used for stable isotope Strasser techniques in research. So, mass spectrometer is a very useful instrument in a good organic laboratory.

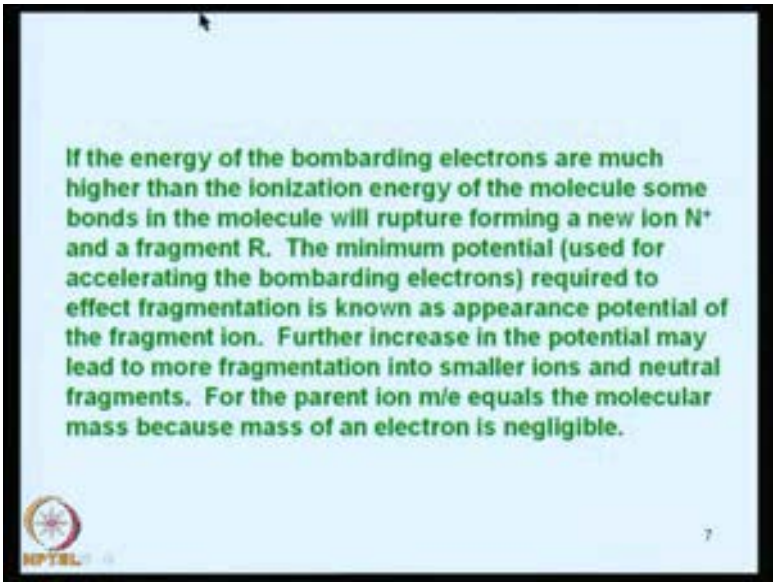
(Refer Slide Time: 20:04)



So, the, essentially the mass spectrometer is the, what it does this in a mass spectrometer, a molecule m is bombarded with high energy electrons of the order of about 70 ev which

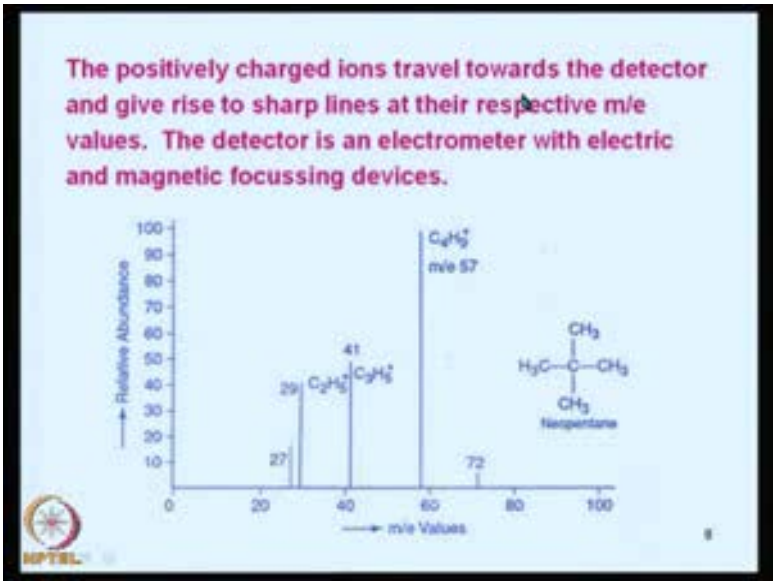
corresponds to approximately 6688 k J per mole. This is the typical bond energy of the organic molecules; that means, in mass spectrometry, you have to break the bonds, then only you will get different ions, molecular ions. So, when the energy of the bombarding electron is equal to the ionization of the molecule, one electron is knocked off from the molecule to produce the parent ion. So, you can see this reaction what I have put here is molecular molecule, one electron knocked off ionization energy. If you produce, then what you get is 1 plus e minus.

(Refer Slide Time: 21:06)



So, if the energy of the bombarding electrons are much higher than the ionization energy of the molecule, sometimes it may be equal; sometimes it may be much higher also. Some bonds in the molecules will rapture all the time any ion and if another fragment is produced. So, new ions are further fragmented. You will get another new ion and further fragmentation. So, the minimum potential use for accelerating the bombarding electrons required to effect fragmentation is known as appearance potential of the fragment ion. So, further increasing the potential may lead to more fragmentation and more smaller ions are produced and neutral fragment also may be produced. For the parent ion m by e equals the molecular weight because the mass of the electron is negligible.

(Refer Slide Time: 22:17)

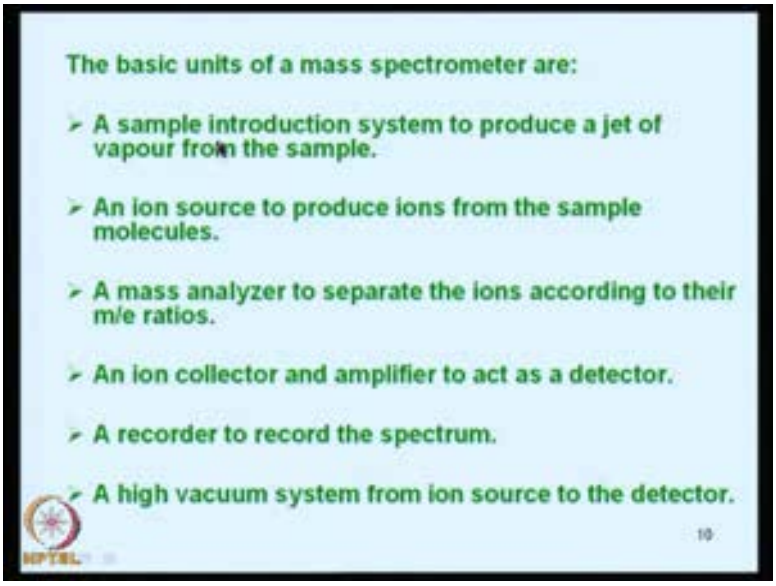


Now, the positively charged ions, if put them in a magnet or a electro magnet, the charged ions travels towards the detector and give a rise to sharp lines at the respective m by e values. The detector is basically an Electrometer with electrical, with electric and magnetic focusing device; that means, the through the magnet, the velocities of the mass ions will be changing and the one with the highest mass would be moving much more slowly than the one with the lowest mass.

Here I am showing you a mass typical mass spectrum for neo-pentane. What we have discussed earlier that several species are there, and here, you would that mass molecular mass highest peak is 72, but the maximum intensity peak is corresponds to m by e ratio of 57. Then there are C3H5 is 41, C2H5 is 29 like that. Other peaks, other peaks are obtained, this is, how a mass spectrometer mass spectrum of a compound looks like.

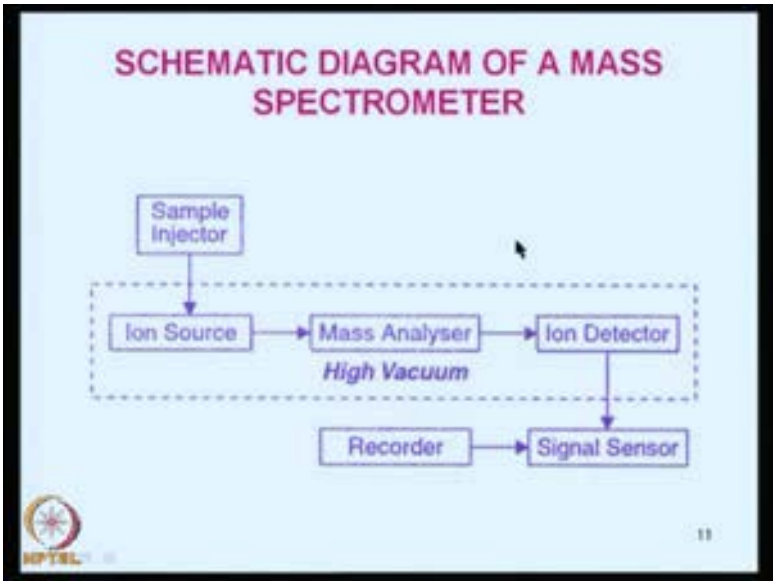
So, from the patterns obtained from pure compounds and that given by the sample considerable information, lot of information can be generated regarding the structure or composition of the sample. It is possible to obtain the spectra of the negative ions, but electrically neutral fragments if they are produced during the bombardment, they cannot be detected in a mass spectrometer. So, we have to remember that.

(Refer Slide Time: 24:17)



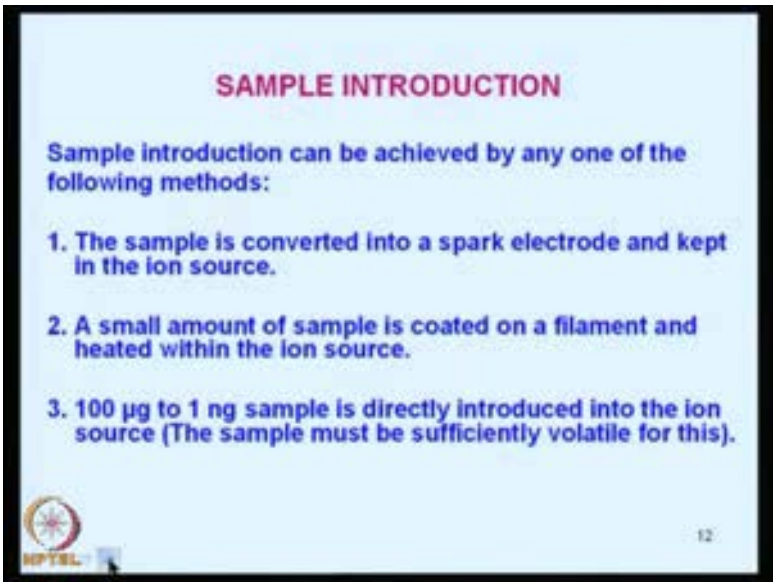
So, the basic unit of a mass spectrometers are a sample introduction system, in which, you introduce a small amount of the sample as a jet of vapor or a liquid from the sample. Then you need an ion source to produce the ions from the sample molecules; then you need a mass analyzer to separate the ions according to the m by e ratios, and you need an ion collector and amplifier to act as a detector, and probably, because ions are produced in large numbers and large quantities you need a recorder automatic recorder; that means you cannot be done manually, and high vacuum system from ion source to the detector is an essential component of a mass spectrometer.

(Refer Slide Time: 25:16)



So, this is the schematic diagram of mass spectrometer. Here, the sample injector is here; it is go it goes into the ion source. We have a high vacuum, mass analyzer and then ion detector, signal sensor and a recorder. This is a very simple schematic diagram.

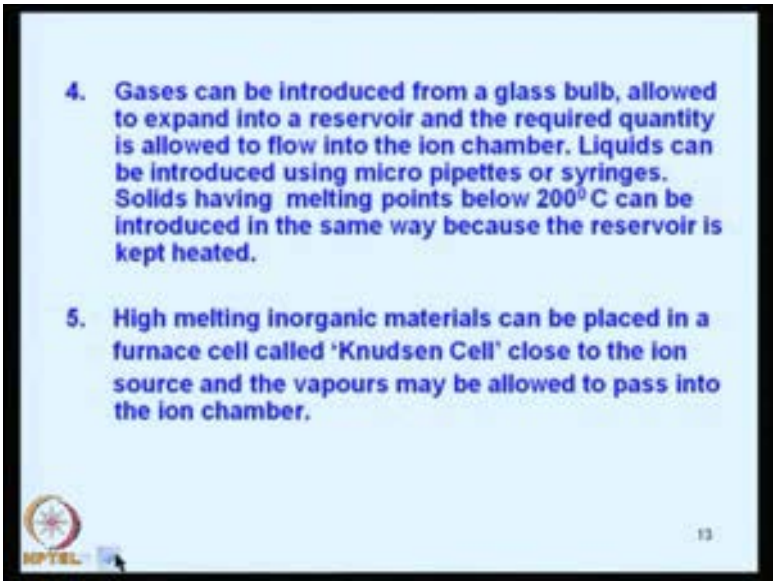
(Refer Slide Time: 25:34)



So, let us discuss about the different aspects of the mass spectrometer. So, as far as sample introduction is concerned, we can say that it should be achieved by any one of the methods what I have showing you in this slide.

One is the sample is converted into a spark electrode and kept in the ion source. A small amount of the sample can be quoted on a filament and you can heat the filament within the ion source or you can take 100 to 100 microgram to 1 nanogram of the sample. You can directly introduce into the ion source, and for this, the sample must be sufficiently volatile; otherwise, you will not be able to handle if the substance is having very high molecular weight and it cannot be volatilized easily, etcetera.

(Refer Slide Time: 26:30)



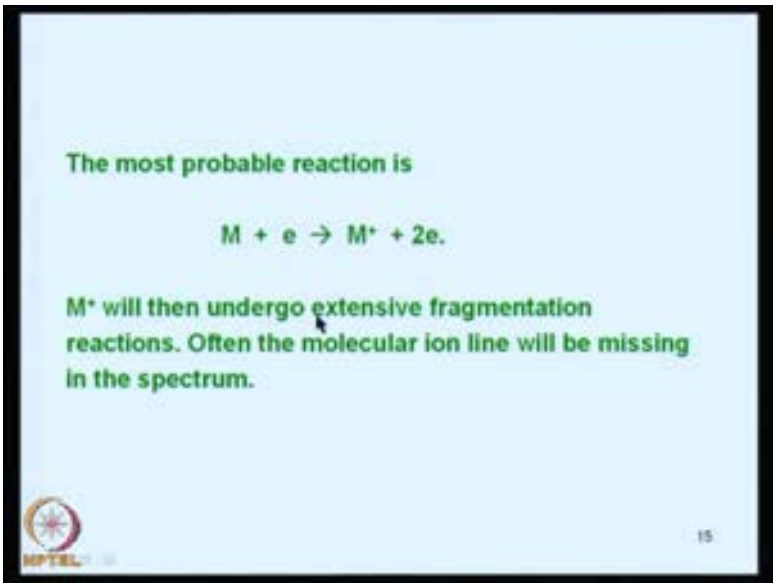
So, what about gases? The gases can be introduced from a glass bulb allowed. You can introduce them in a glass bulb and allowed it to expand into a reserve wire and the required quantity is allowed to flow into the ion chamber using a valve. So, you can control how much of the sample flows into the ion analyzer if you are introducing the gas directly. So, liquids can be introduced using micro pipettes or even simple syringes and solids having melting point above 200 degree centigrade. They should be introduced in the same way because the reserve wire is kept heated.

So, you can dissolve it and then put, put, the sample solids. You can dissolve the solid in a liquid and introduce it as a liquid. So, high melting in inorganic materials can also be directly placed in a furnace called as Knudsen cell and close to the ion source and the vapors may be allowed to pass into the ion chamber. These are the different ways in which we can introduce the sample.

So, in the, now, when we come to the ion source, what I would like to say is the samples that are sufficiently volatile may be produced either by electron impact or by chemical ionization. You can bombard them with the electrons or simply keep on heating it until you get the ionized sample. That is known as chemical ionization. The electron impact technique is basically a heated tungsten filament emitting electrons which are accelerated by applying a potential difference of about 70 volts. The kinetic energy of the electrons

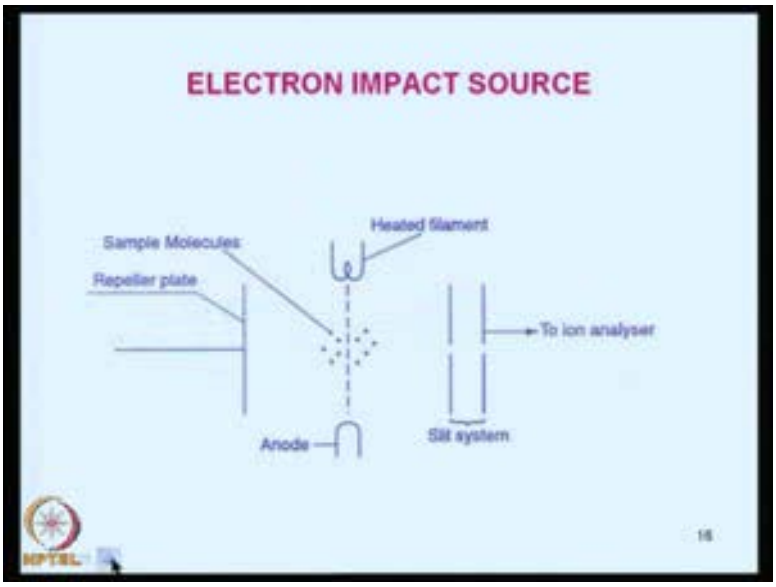
will be equal to seventy electron volts which is sufficient to analyze ionize rather most of the organic molecules.

(Refer Slide Time: 28:56)



So, you can, the most probable reaction is like this that m plus e equal to m plus m 2 e m plus will then undergo extensive fragmentation reactions. Often the molecular ion line will be missing in the spectrum that we should be aware.

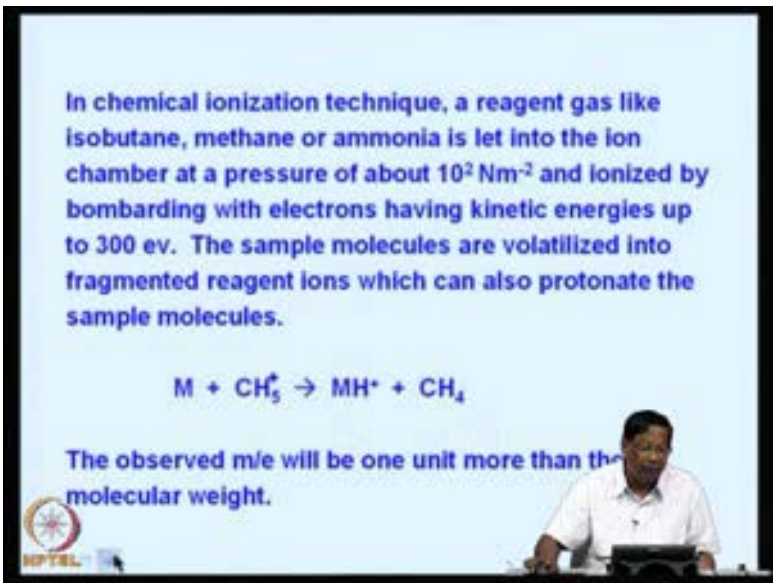
(Refer Slide Time: 29:08)



So, in the electron impact source, what we have is the heated filament is here and this is the anode and sample molecules are introduced somewhere here and the electrons will

get bombarded. Electrons will bombard the molecules and then there is a Repeller plate; sample molecules are here, and then, there is a slit system, and through which, it goes to the molecular ions will travel towards the ion analyzer. This is basically a very simple an schematic diagram for the production of the ions..

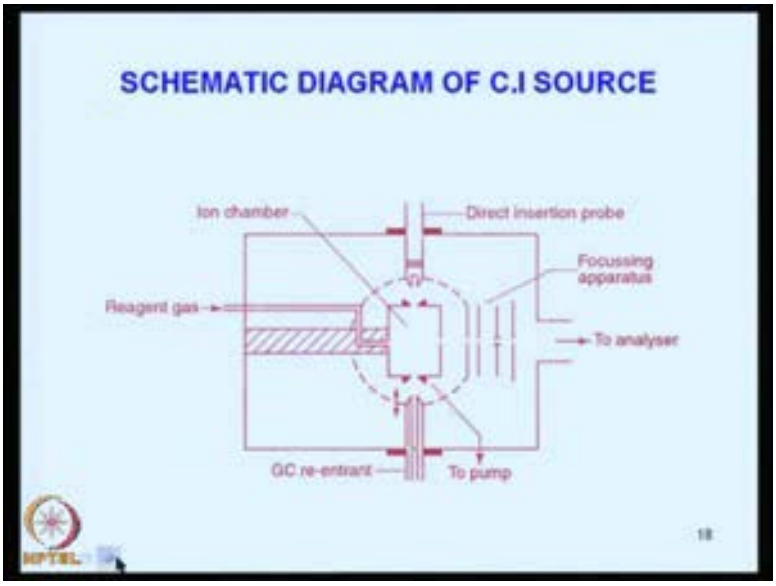
(Refer Slide Time: 29:48)



In chemical ionization technique, a reagent gas is required, that is, you can use isobutane you can use isobutane or methane or ammonia and you have to let it into the ion chamber at a pressure of about 10 raise to 2 Newton per square meter and ionized by bombarding the electrons having kinetic energies up to 300 electron volts. The sample molecules are volatilized into fragmented regent ions which can also protonate the sample molecules.

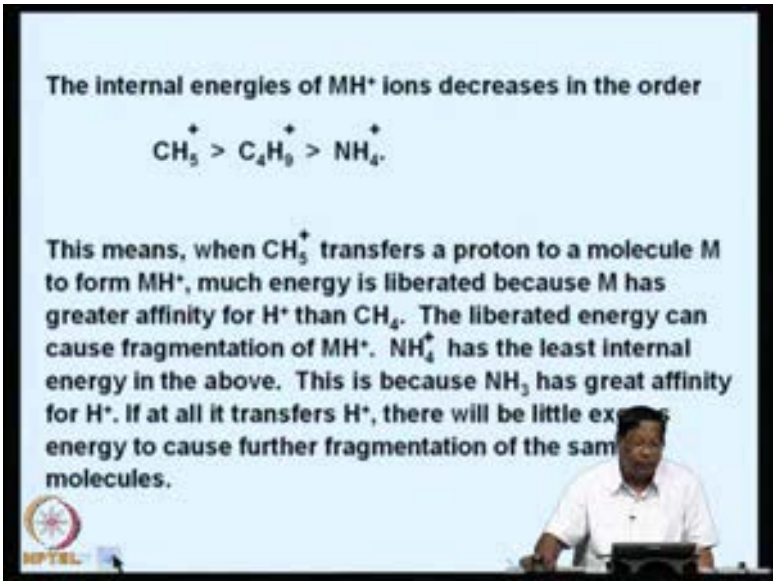
So, for example, if you have a molecule like this and then you have CH5 molecule at ion, then it can pick up one hydrogen from here producing MH and CH4. The observed m by e unit will be one unit more than the molecular weight. Such a possibility one has to be aware.

(Refer Slide Time: 30:54)



And the, this is the schematic diagram of a C I - chemical ionization – source. Here, the reagent gas is introduced like this and this is the ion chamber and this is the direct insertion probe through which the sample is this thing and then introduced and this is the g c re entrant and this goes to a pump and we have a slit and analyzer focusing operators and all other things will be in place.

(Refer Slide Time: 31:30)

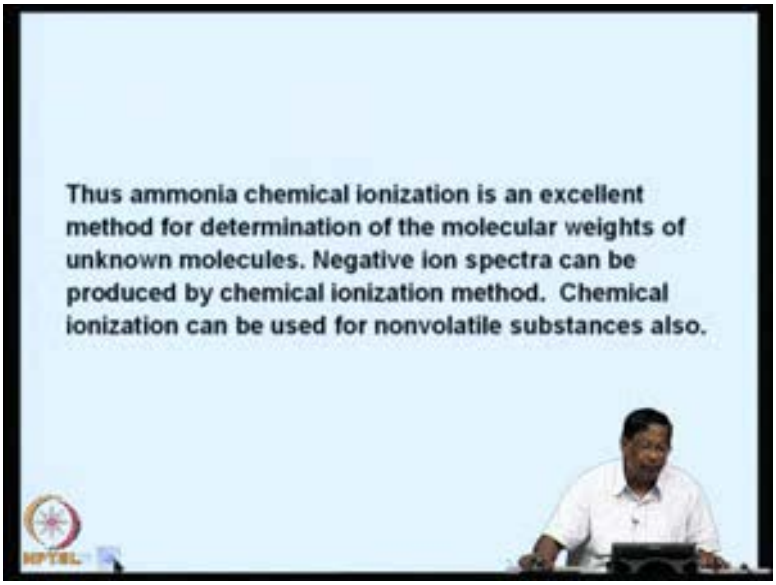


So, the internal energies of the MH ions increase in the order of increasing molecular weight. For example, this is CH5 ion is higher than C4H nine and which is much higher

than NH4 ion; this means when CH5plus transfers and proton to molecule M to form MH plus much energy is liberated because m has grater affinity for h plus than methane because methane cannot pick up another hydrogen atom.

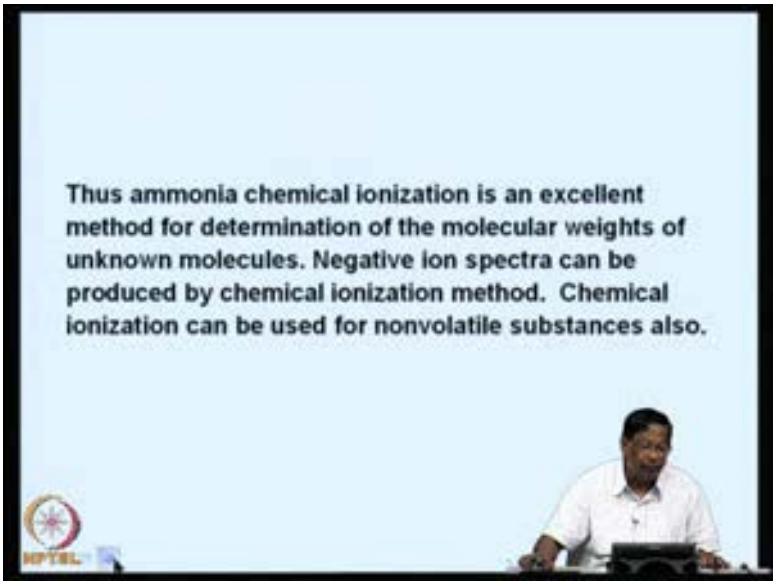
So, the liberated energy can cause fragmentation of the m h plus itself and NH4 plus has the least internal energy in the above list, that is, in this list. So, this is because ammonia has great affinity for H plus; it just picks up another hydrogen atom to form NH4 plus. So, if at all if it transfers H plus, there will be little excess energy to cause further fragmentation of the sample molecules. Therefore, ammonia is the least prefer one compare to butane.

(Refer Slide Time: 32:49)



So, the ammonia chemical ionization is basically an excellent method for the determination of the molecular weights of unknown molecules. Negative ion spectra can be produced by chemical ionization method. And chemical ionization can be used for nonvolatile substances also.

(Refer Slide Time: 33:15)

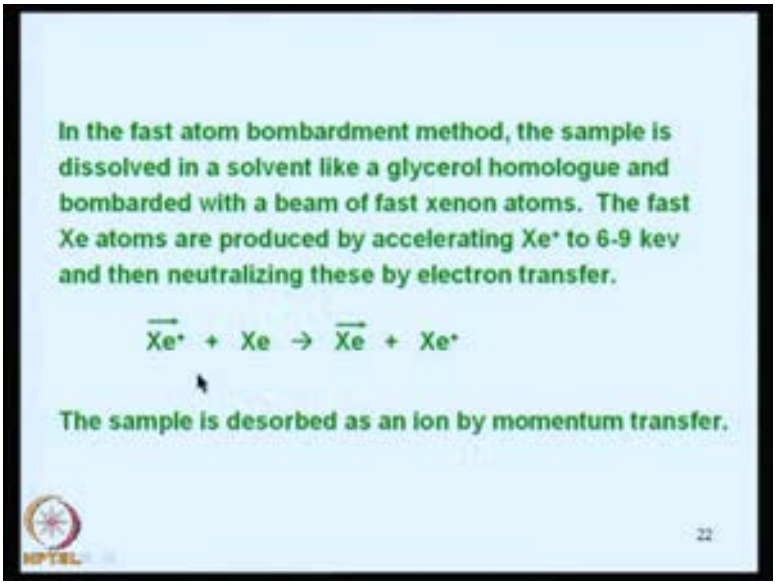


For nonvolatile substances, ionization methods basically include field desorption, that is, this is field desorption you can use or fast atom bombardment known as f a b or californium plasma desorption. That is known as c f b d or you can use laser desorption photonizer different techniques are there to produce ions. In the field desorption method, a solution of the sample is simply smeared on a heated wire maintained around 8000 volts.

So, the electrons are transferred from the sample to the wire metals and positive ions are desorbed by the electrostatic repulsion. So, the ions may collide to form m h plus. So, once m h plus is produced, then we have the weight (( )) for the production of other molecular ions. So, in laser desorption, the sample is eradiated with a laser beam. Here, the energy get absorbed by the sample; it volatilizes and ionizes it. So, it is not possible to go more into details because basically these are all specialized instruments and each instrument will have its own, separate way of, separate way of producing the mass ions.

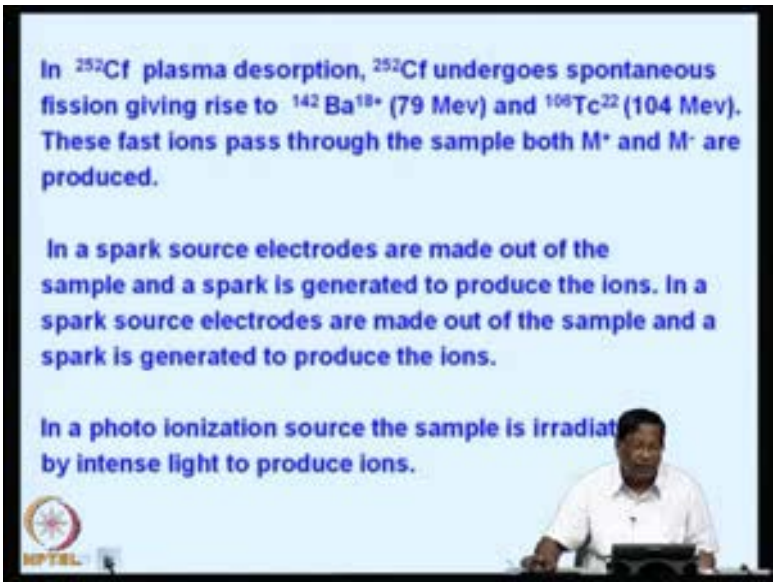
So, the, another technique that we had discussed is fast ion bombardment. Here, the sample is resolved in a solvent like a glycerol homolog and bombarded with a beam of xenon atoms. The fast xenon atoms are produced by accelerating the xenon ions to about 6.9 electron volt kilo electron volts and then neutralizing these with the electronic electron transfer.

(Refer Slide Time: 35:37)



You can take a look at this slide. What I am showing you here is xenon ions can combined with another xenon to produce xenon ions and xenon molecules. So, the only the momentum is transferred here basically and the sample is desorbed as an ion by the momentum transfer rather than the production of separate ions.

(Refer Slide Time: 36:00)



Now, we have also discussed the californium atom bombardment, that is, we use 252Cf plasma desorption, and in this, 252Cf undergoes spontaneous fission giving rise to 142 Ba - barium - 18plus that 79 Mev and another atom that is produces is 106Tc22; this106

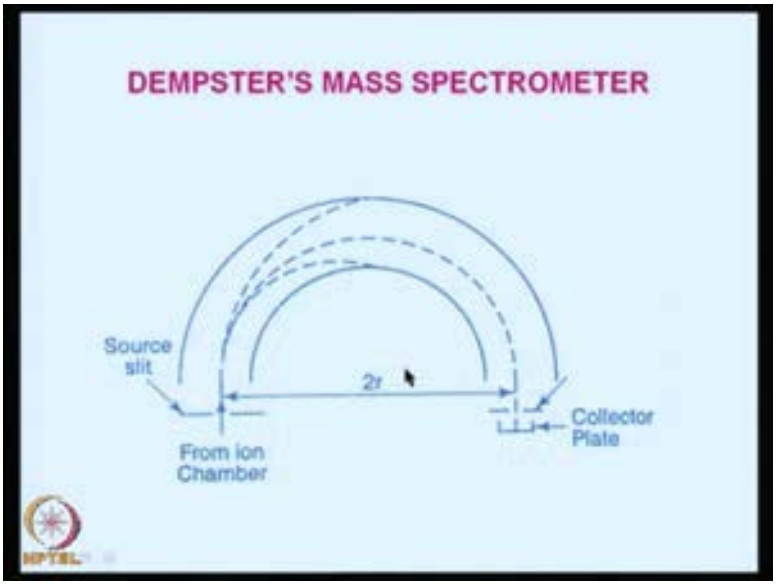
refers to the atomic weight and this happens at 104 Mev. These fast ions what they do is they pass through the sample both m plus and m minus are produced; that means, they ionized the whole sample in this is another way of producing the atoms.

So, in a spark source electrodes are made out of the sample and a spark is generated to produce the ions. In a spark source electrodes are made out of the sample; that means, just like what we have discussed earlier I C P - Inductive couple plasma - you take two electrodes in which the samples are put and brought together under high voltage. A similar technique is employed here and spark is generated to produce the ions. In the spark source, the electrodes themselves must be made of the sample and or you can put the sample in a cavity in an electrode and bring the sparks nearer, and at some stage, you will get a spark and high energy is generated and the ions will be produced.

So, another technique is photo ionization. Here, the source, in this photo ionization source, the sample is irradiated by intense light to produce the ions. So, all in all, there are different ways of, producing the, producing the molecular ions and fragment ions depending upon the type of work what you usually do. And if you are using a mass spectrometer in which radioactive substances are involved, then it is better to go for two fifty two californium. Like that one can use different kinds of mass spectrometers ion producer's mechanisms.

And the ions from the mass analyzer ion source are usually repelled by electron repeller electrodes, and which are, if they are repelled by with the same force by which they are generated, then they get accelerated and get injected into the mass analyzer. Here, the ions are separated according to the m by e ratio as we have discussed earlier. This principal is illustrated by Dempster's mass spectrometer. Very simple mass spectrometer have been constructed right from about eighteen fifties, and now a days the instrumentation in mass spectrometer has reached a very high level. And in Dempster's mass spectrometer, positively charged ions entering from the ion source are accelerated by an electrostatic field. So, a magnetic field edge is applied in a perpendicular direction. So, the ions do get accelerated.

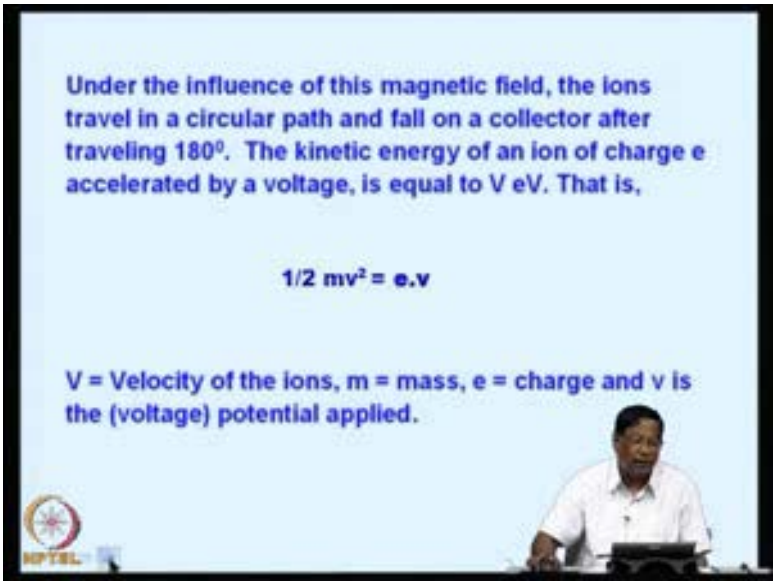
(Refer Slide Time: 39:58)



And this is the next slide shows you that a Dempster's mass spectrometer. Here, we have a Source slit; that means, we assume that all the ion production is over, and from the ion chamber, the ions are entering a magnet, and here, there is a collector plate. The diameter of this is 2 r and electrons will travel through the magnet and fall on to the Collector plate.

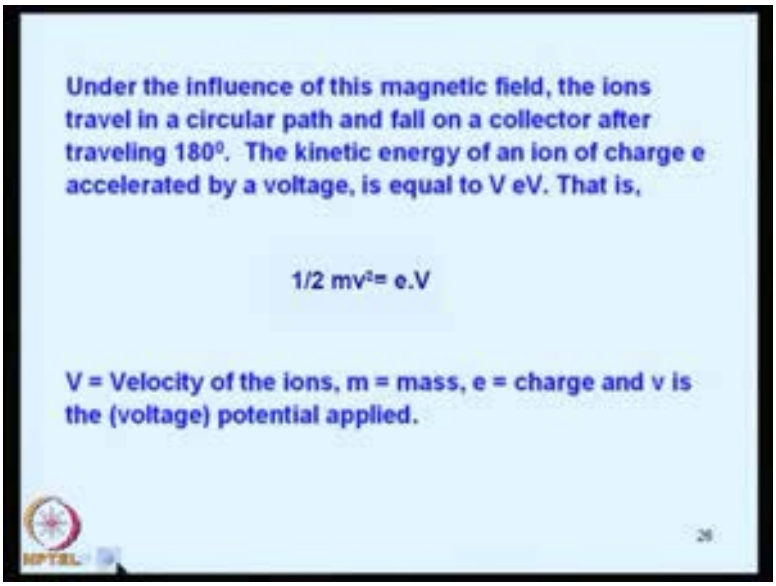
So, the ones which are having exact path will get, through to, through the detector, but others are not. So, at as you increase the collector plate voltage, you will be able to collect this one, this one, this one, that separate electrode electronic values separate voltages.

(Refer Slide Time: 40:57)



So, under the influence of the magnetic field, the ions travel in a circular path and fall on a collector after travelling 180 degrees. So, the kinetic energy of the ion of charge e accelerated by a voltage, is equal to v volts electron volts. So, that is ½ mv square is equal to e V. That is the equation what we use in this slide.

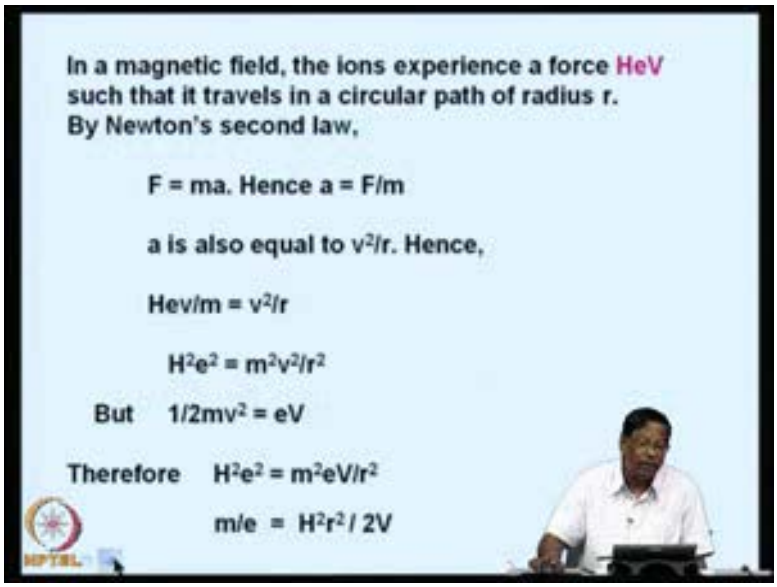
(Refer Slide Time: 41:37)



So, we want make sure that the voltage ½ mv square. This is the momentum; this is the electronic voltage, and where V is the velocity of, the, this is small v and this is the

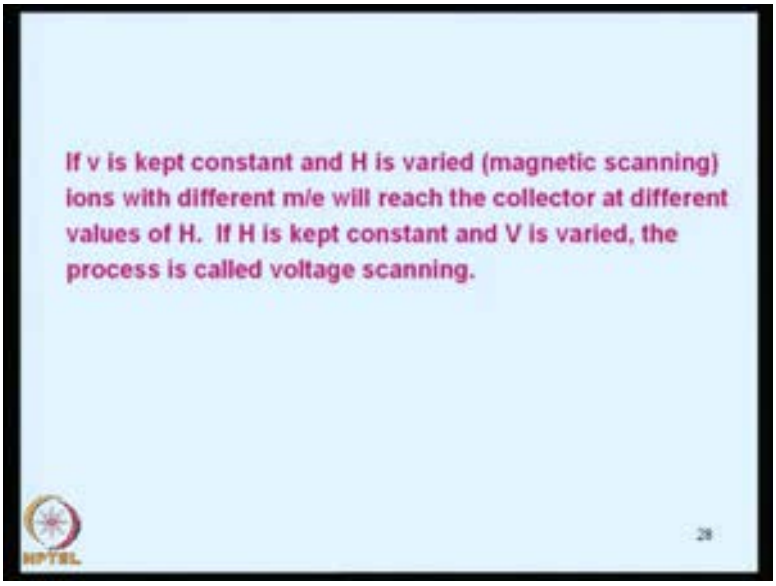
voltage, sorry, and V is the velocity of the ions; m is the mass and e is the charge and v is the potential.

(Refer Slide Time: 42:02)



So, at a time one molecular ion will be produced and that will be reaching the electrode collector plate. In a magnetic field, the ions experience a force HeV such that it travels in a circular path of the radius r, and by Newton's second law, you can write force is equal to mass into acceleration and acceleration should be F/m. So, a is also equal to v square by r. So, we compare these two equations, that is, v square by r should be equal to H into ev by m, and this will, if you work out a little bit, so, here, we take the squares and then 1 by 2 square if we generate, you will see that m by e value corresponds to H square r square divided by 2V.

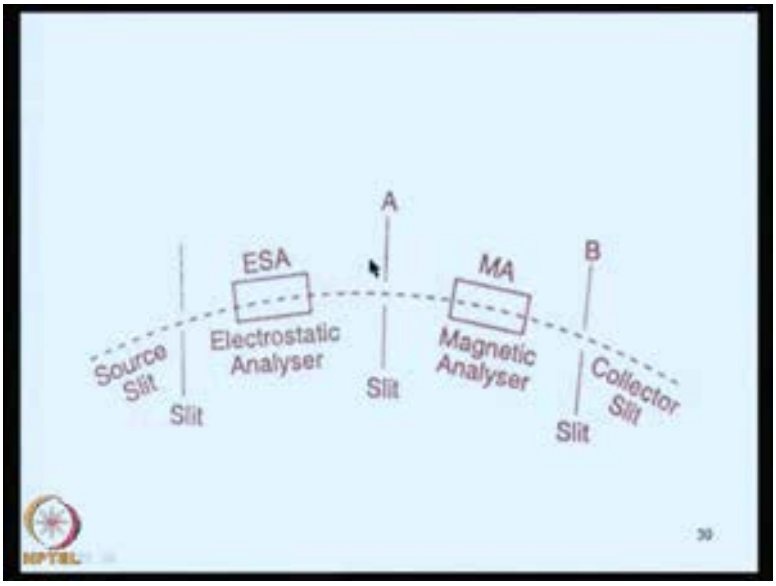
(Refer Slide Time: 43:10)



And this gives us a maximum, an expression for collecting the mass of a particular ion. So, if v step constant and magnetic field is varied, ions with different m by e will reach the collector at different values and different values of the magnetic field. So, if H is kept constant, you can, you have two choices - one is you can increase the magnetic; keep the v velocity constant and increase the magnetic field from 0 to 70 or you can keep the H magnetic field constant and increase the change the velocities. The process is called voltage scan. So, you can change the, by changing the voltage, you can change the velocity. This is essentially the cracks of mass spectrometry.

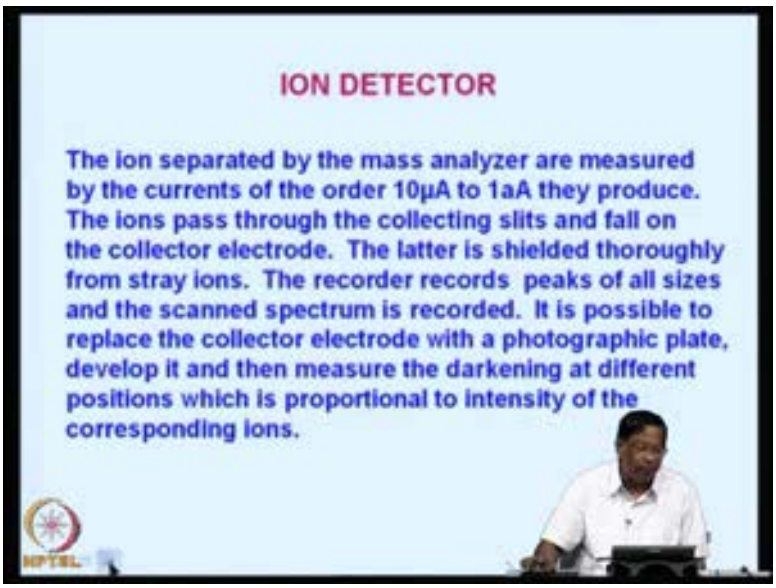
So, what I would like to tell you at this stage is due to variations in the kinetic energy of the ions entering the mass spectrometer. That is the magnetic field, etcetera. From the ion source, the resolution of the Dempster's mass spectrometer is limited because the kinetic energy is not uniform all the time. To overcome this problem, the ions are pass through an electric field prior to the magnetic field. So, what does, what does it mean? We pass the ions through an electric field first prior to magnetic field, and, the, here, the ions are focused and then pass through a slit into the magnetic sector. So, that means focusing is always is already done. This results in higher resolution that can distinguish m by e differences of the order of 0.01 mass unit. That is good because it will give you a way of reproducing the mass spectrum within the…

(Refer Slide Time: 45:36)



So, here is again I have put the modified arrangement. One is the ion source. I have an electrostatic analyzer. This is the slit, and then, after the electrical electrostatic analyzer, we pass it through the magnetic analyzer, that is, m a and then on to the collector slit.

(Refer Slide Time: 45:57)



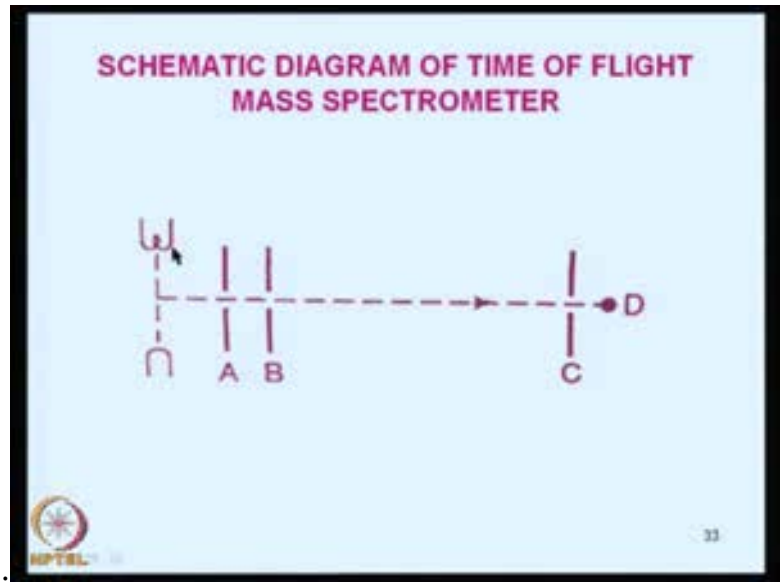
So, this way, we can differentiate between point zero one mass unit very comfortably. Now, once you are able to collect the separated mass of the mass ion from a given compound and sample, the ions separated by the mass analyzer must be measured how? It must be measured by the current generated when the ions fall on to the detector. So,

This order is approximately ten micro amperes to one milliamps they produce. The ions pass through the collecting units and fall on to the collector electrode. So, the later, that is, the collecting electrode is shielded thoroughly by the stray ion. That is very important. Stray ion should not be coming and hitting the collector plate at the same time. So, that will not lead to good mass spectrum.

So, the recorder records peaks of all sizes and the scan spectrum is opted. So, it is more essential that stray ion should not be collected, they should, there must be a mechanism to remove all the stray ions before it hits the collector electrode. So, it is possible to replace the collector electrode with a photographic plate and develop it and then measure the darkening at different positions, which is proportional to the intensity of the corresponding ion. This is another way of detecting and determining the mass spectrum.

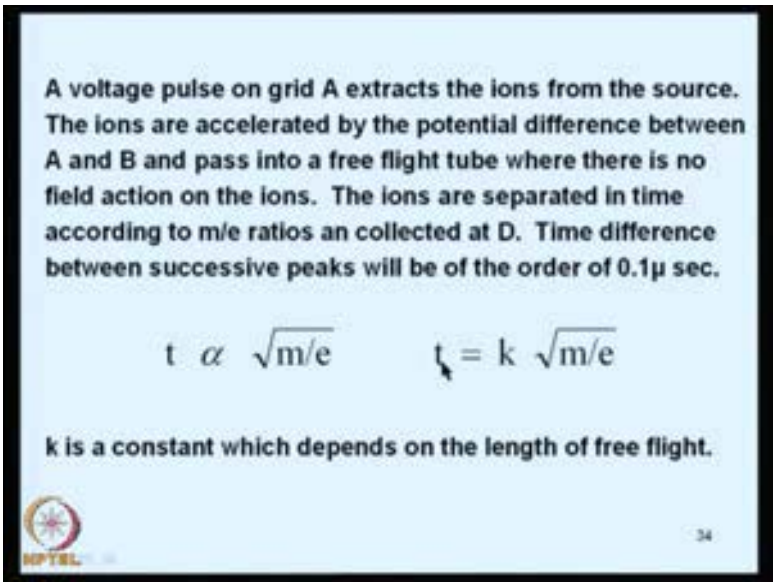
So, the, let us discuss a little about the time of light mass spectrometers. So, in a time of light mass spectrometer, all the ions emerge simultaneously from the electrostatic field with the same energy. So, the ions with the largest mass will have the lowest velocity. So, they can, they take, the, they take longer time to reach the detector collector plate; that means, to travel the same distance, the molecular ions with the maximum, with the maximum, molecular weight will take longer; the lighter ones will travel faster. Essentially, this is the principal of the time of the flight mass spectrometer.

(Refer Slide Time: 48:48)



So, schematic diagram of the time of mass spectrometer I am showing you here. It is very simple schematic diagram. This is the (( )) and then slits. One is electrostatic and then and then the collector plate and the detector, very simple.

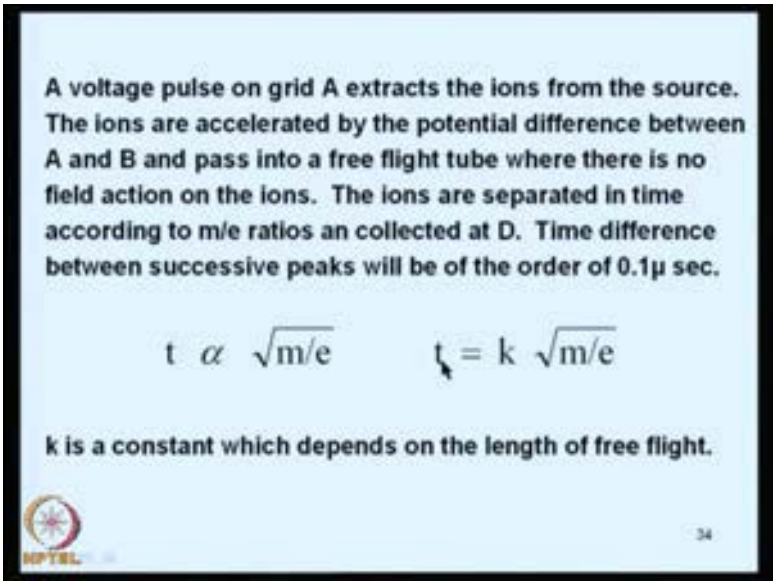
(Refer Slide Time: 49:02)



So, actually, when I say it is very simple, it means that the principle is simple, but the instrumentation. Instrumentation is much more complicated involving the management of the bombardment source and then collector electrode, voltage, etcetera.

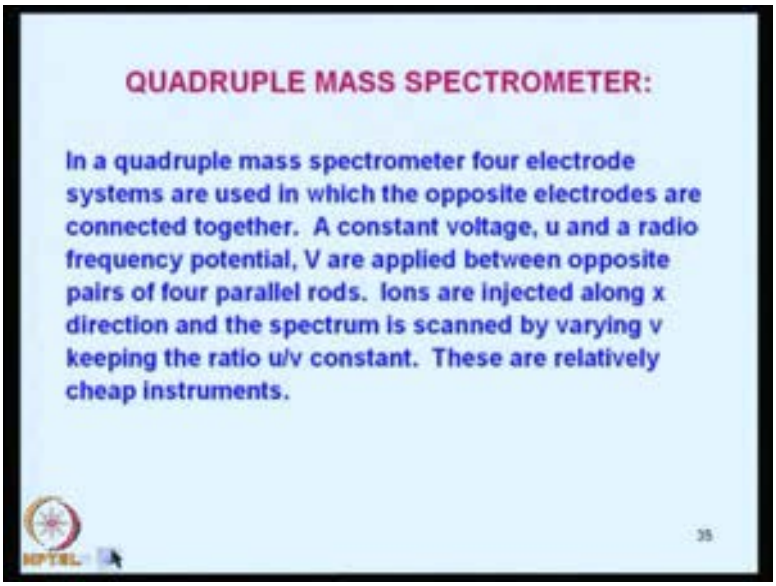
The chemistry part is only related to require is the sample introduction and then interpretation. The all other things are basically instrumentation controlled and most of these things are nowadays microprocessor controlled. So, a voltage pulse on, grid extra, on grid a extra x the ions from the source. Here we need a voltage pulse to extract the ions. The ions are accelerated by the potential difference between the two and pass into a free flight tube round tube where there is no field action on the ions. The ions are separated in time as they travel depending upon the m by e ratios and collected at D. That is the collector plate. So, the time difference between the successive peaks should be minimum 0.1 micro second. So, you can write an equation like this t is proportional to square rout of m by e. That is the equation.

(Refer Slide Time: 49:02)



We will always can be very simply written like this, that is, t is proportional to square route of m by e and t is also equal to you can put a constant and square rout of m by e, and the - where k is a constant which depends on the length of the free flight. So, this is a very simple equation.

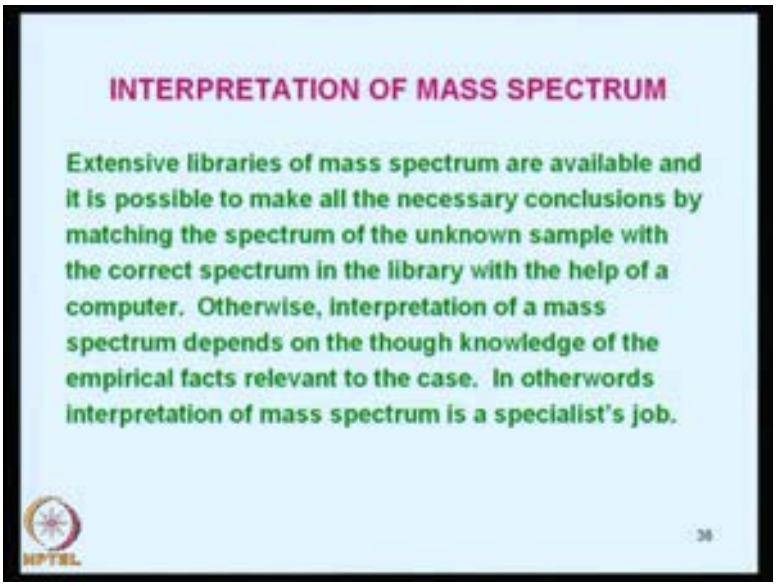
. (Refer Slide Time: 51:08)



And then we can discuss a little about quadruple mass spectrometers. So, a quadruple mass spectrometer has, four electro, four electrode systems are used in which the opposite electrodes are connected together. So, a constant voltage u and a radio

frequency potential is require and V voltage is applied between the opposite pairs of four parallel rods. Ions are injected along the x direction and the spectrum is scan by varying v voltage keeping the u by v ratio constant.

(Refer Slide Time: 51:57)



So, these are relatively cheaper instruments with compare to time of light instruments. So, this is essentially about the instrumentation, but what I would like to tell you again in, the, this time is, that the mass spectrometry and infrared spectrometry are basically user oriented instruments. And the more you work on these instruments, the more expertise you will gain and no amount of teaching will make you an expert on the interpretation part. So, the interpretation of mass spectrum is a different subject by itself and one can take (( )) in the fact that as you keep on using an mass spectrometer, your expertise will improve.

So, extensive libraries of mass spectrum are available now a days, that is, data bases and it is possible to make all the necessary conclusion by matching the spectrum of an unknown compound with the correct spectrum available in the library, and with the help of a computer, the whole job become simpler. Otherwise, interpretation of mass spectrum depends on the thorough knowledge of the empirical facts relevant to the case. In other words, interpretation of mass spectrum is always a specialist job depending upon the type of compounds, what you are handling.

So, I would not well more of this aspect, because the more I teach, the more you will get into the chemistry of the subject and, it may, it is not relevant for this present course. So, for the, at this stage, what I would like to say is the instrumentation of mass spectrometry is essentially a very simple system but more involve with respect to the preparation of the magnet ion bombard source and detector plate etcetera, but the interpretation of the instrumentation, remains, remains the domain of the electrical engineers and mechanical engineers and maintenance engineers.

The use and application of mass spectra are always in the chemists domain. So, the more you would like to know, the more you have to use the instrument more and then you will be able to get the require expertise. For the, for brevity, for the sake of brevity, I have included this mass spectrum for this course just to give you an insight into how a mass spectrometer works and what are the typical uses of a mass spectrometer and, how we can, it will give you an insight when you should use a mass spectrometer.

Basically, what you should be doing is - if you are handling typically organic compounds, then you can use mass spectrometer, for the, for the, for following a chemical reaction and the mass spectral data can be used to interpret the reaction mechanism or the, the, generation of the different ions from the molecule that can be use, that it can be used. And sometimes, mass spectrometers are also coupled with gas chromatographs or high pressure liquid chromatographs so that the, the, separated compounds from gas chromatography or h p l c can be directly automatically injected into a mass spectrometer to get the typical separations as well as identification of the substances.

So, I will stop here. And in the next class, what we will do is - we will take a similar look on the instrumentation of n m r technique, which is another technique very similar to this, but the interpretation and the usage are more limited to organic chemist rather than analytical scientist. But as for the sake of brevity, we will continue our discussion on this n m r in the next class.