Indian Institute of Technology
Kanpur

NP-TEL
National Programme
On
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-24

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So we have been discussing about different advanced surface characterization techniques for the last four or five and more seven lectures.

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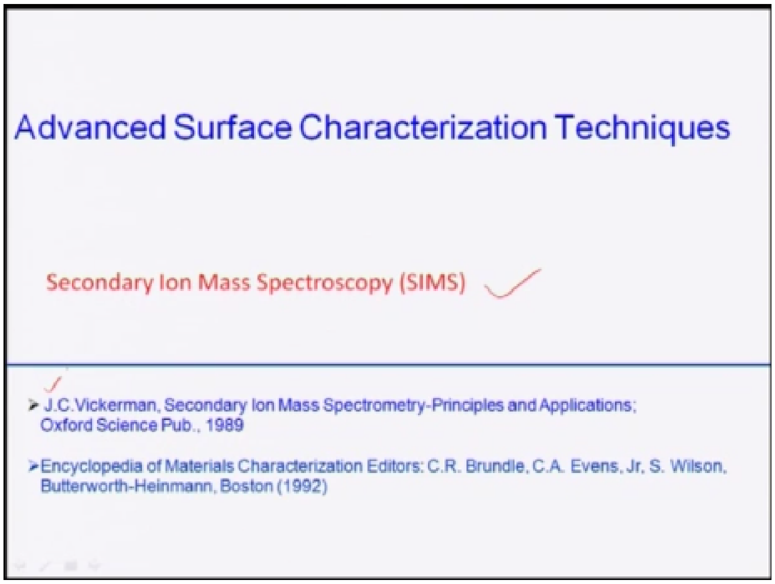

Advanced Surface Characterization Techniques

Secondary Ion Mass Spectroscopy (SIMS) ✓

- J.C.Vickerman, Secondary Ion Mass Spectrometry-Principles and Applications; Oxford Science Pub., 1989
- Encyclopedia of Materials Characterization Editors: C.R. Brundle, C.A. Evens, Jr, S. Wilson, Butterworth-Heinmann, Boston (1992)

The last technique which I am going to discuss in detail is known as secondary ion mass spectroscopy. In the literature it is always written as SIMS being the acronym for secondary ion mass spectroscopy. It is very advanced technique and very few laboratories in India have access to this technique. As far as I know all the laboratories access to the atomic energies like BRC or Agica, they have access to these facilities.

But still for the understanding of different students, we need to discuss this technique in detail. The literature is very well known in these topics. The most important books on which literatures are available are listed at the bottom. First one is by J.C. Vickerman. Second one is again the encyclopedia or the material characterization edited by Brundle and Evens and Wilson. These two books are easily available in different libraries, so you can have access.

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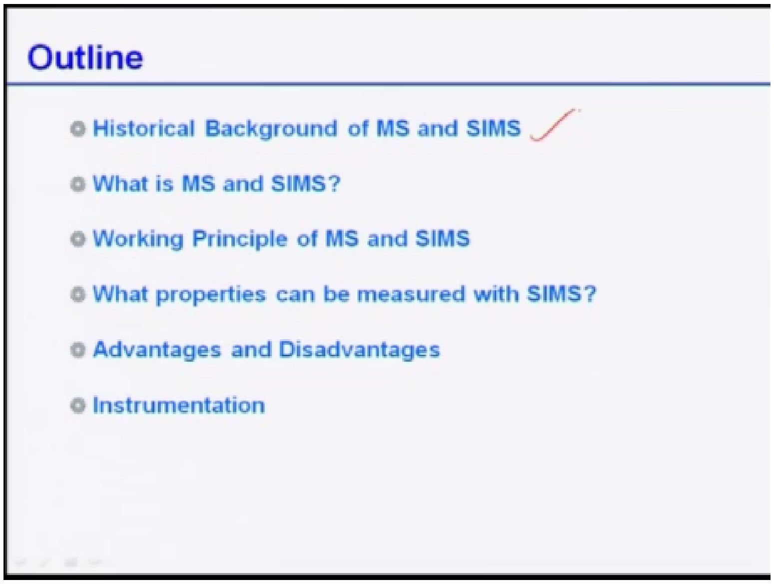

Outline

- Historical Background of MS and SIMS
- What is MS and SIMS?
- Working Principle of MS and SIMS
- What properties can be measured with SIMS?
- Advantages and Disadvantages
- Instrumentation

The outline of this presentation is as follows. First I am going to discuss about historical background of SIMS, but before I discuss about historical background of SIMS I must talk about the mass spectroscopy per se. Then I am going to talk about the difference between the MS and the SIMS and most typically what are these two techniques are, so that you can get a feeling of mass spectroscopy and secondary ion mass spectroscopy.

Obviously these two techniques are related. Followed by I will discuss the working principle of both the techniques and then I am going to talk about different measurements which can be done by SIMS, also lastly the advantage, disadvantage and some amount of instrumentations.

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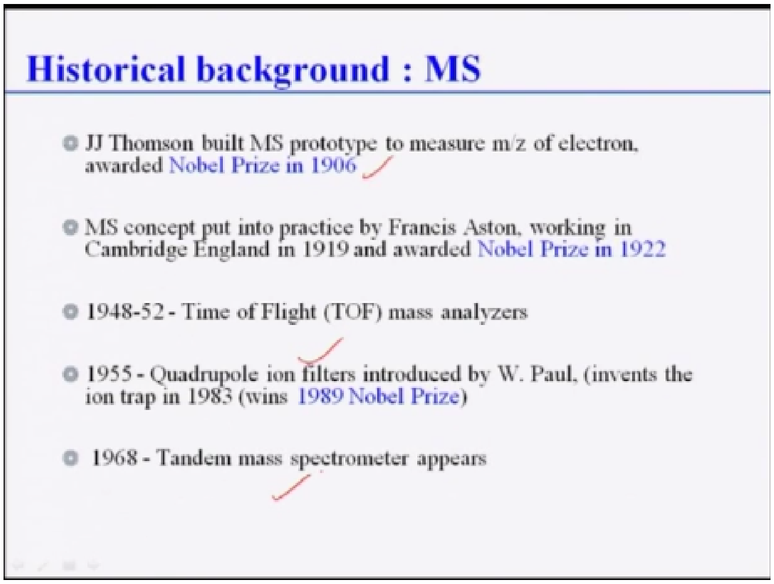

Historical background : MS

- JJ Thomson built MS prototype to measure m/z of electron, awarded Nobel Prize in 1906
- MS concept put into practice by Francis Aston, working in Cambridge England in 1919 and awarded Nobel Prize in 1922
- 1948-52 - Time of Flight (TOF) mass analyzers
- 1955 - Quadrupole ion filters introduced by W. Paul, (invents the ion trap in 1983 (wins 1989 Nobel Prize)
- 1968 - Tandem mass spectrometer appears

As you know it all started in about 100, 10 years back by Sir JJ Thomson who first basically built the prototype of mass spectroscopy to measure the M/Z of an electron, mass/species charge. And as you know he was awarded a Nobel Prize in 1906 for his discovery and for many other things which he has made. Thus, basically the first concept of mass spectroscopy came into practice by a gentleman known Francis Aston who was working in Cambridge in England.

And he actually first principle of concept of mass spectroscopy was put forward into practice by him, and he was awarded a Nobel Prize in the year 1922. Then it saw a huge effort to make the mass spectroscopy popular. Different kinds of mass spectroscopic techniques came into picture. But the real problem in dealing with mass spectroscopy was the vacuum systems. In early 20th century, basically 10-19, 30, in 1935 the vacuum technology was not so well known.

So the technique has not progressed much. Early in 1948 to 52 in a force to Second World War era, the important time of flight Mass Analyzer came into picture and changed the scenario. It was followed by a major discovery again by W. Paul, which leads to Quadrupole ion filters, and this Quadrupole ion filters actually has allowed us to measure the PCS of different mass/z value, m/z values.

And because of this very famous discovery in 1965, W. Paul was awarded a Nobel Prize in 1989. Actually he also invents ion trap in 1983 or information. After that in 1968, it saw the development of Tandem mass spectrometers and secondary ion spectroscopy came little later at about 1980's, when the secondary ion production was possible by different primary ion sources.

To give you better idea of SIMS, the most important problem in developing SIMS was the pumping technology, the vacuum technology as I told already. And that is actually hindered the growth of the SIMS.

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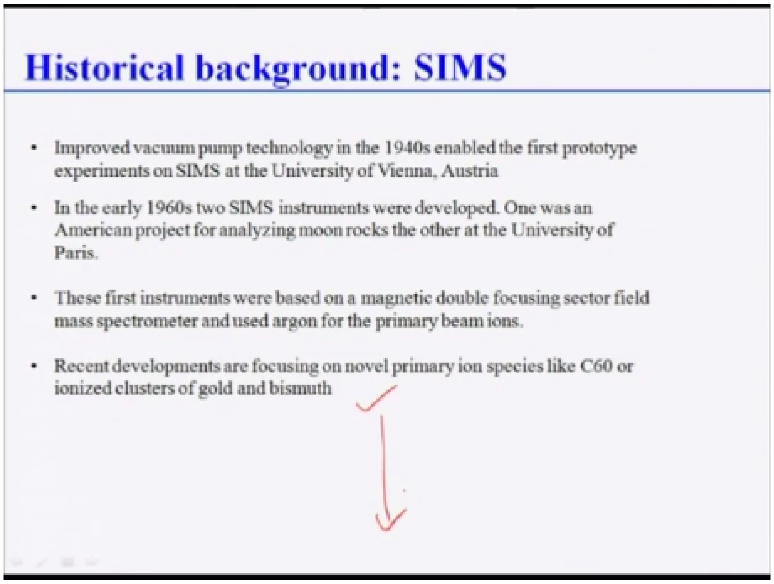

Historical background: SIMS

- Improved vacuum pump technology in the 1940s enabled the first prototype experiments on SIMS at the University of Vienna, Austria
- In the early 1960s two SIMS instruments were developed. One was an American project for analyzing moon rocks the other at the University of Paris.
- These first instruments were based on a magnetic double focusing sector field mass spectrometer and used argon for the primary beam ions.
- Recent developments are focusing on novel primary ion species like C60 or ionized clusters of gold and bismuth

In fact early in 1940s, actually in 1948 or so, the first prototype experiment in SIMS was done at University of Vienna, Austria. In 1960s, two SIMS experiments were developed, but not so good. One was American project for analyzing moon rocks; other was at the University of Paris. These first instruments were based on a magnetic double focusing sector filed mass spectroscopy and used argon as a primary ion beam.

Obviously these things are not known to you I am going to discuss in detail. And then this was followed by recent development on focusing this Nobel primary ion sources, this is just like C60 or ionized clusters of gold and bismuth. And this followed lot of instrumentation in the composition of the technique, and now it is fully automated and comes under cost of about few tens of crores of rupees.

Well what is actually Mass Spectroscopy? Let us see mass now first. Mass Spectrometry or Mass Spectroscopy is basically an analytical technique as any spectroscopic technique. But it measures a different thing.

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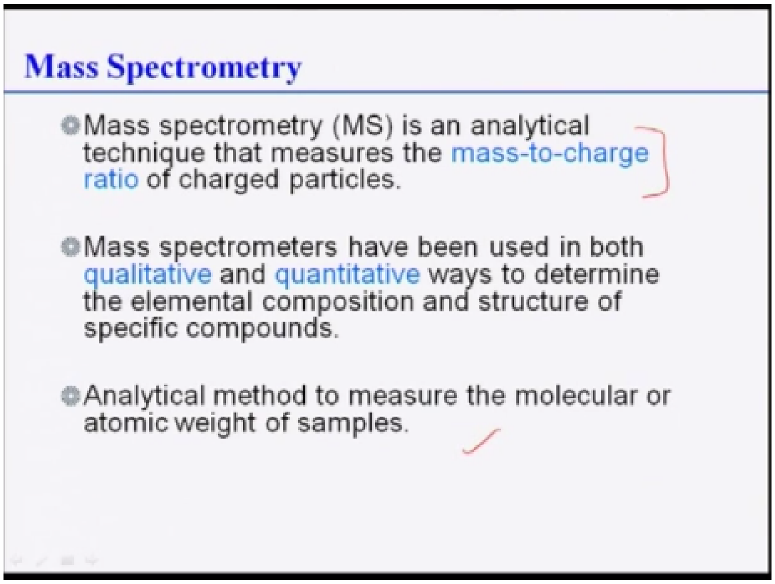

Mass Spectrometry

- Mass spectrometry (MS) is an analytical technique that measures the mass-to-charge ratio of charged particles.
- Mass spectrometers have been used in both qualitative and quantitative ways to determine the elemental composition and structure of specific compounds.
- Analytical method to measure the molecular or atomic weight of samples.

It measures mass to charge ratio of any charged particle. You must remember this. Any mass spectroscopy does not measure mass. It measures mass to the charge ratio of any charged species. So therefore in any sample, whatever you might well you can copy, there is no charged species because the samples will be neutral. You need to create the charged species first and then by using certain technique you can measure this mass to charge ratio.

This is a characteristic of any charge whether it is a single atom ion charge, or it is a multiple ion charge, multiple species charge does not matter, but this is a very characteristic thing. It has used in both qualitative and quantitative analysis. Determine the composition and the structure of specific compounds, not only that it allows us to be used as an analytical method to measure the molecular and atomic weight of the sample.

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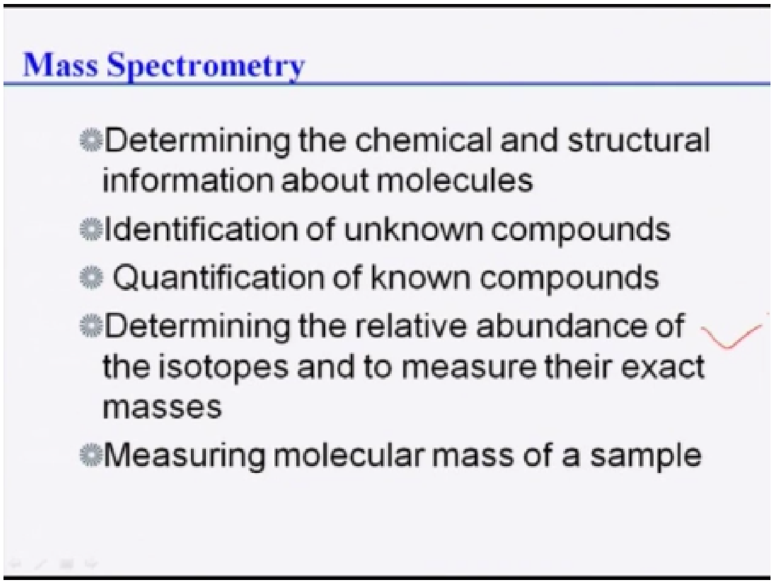

Mass Spectrometry

- Determining the chemical and structural information about molecules
- Identification of unknown compounds
- Quantification of known compounds
- Determining the relative abundance of the isotopes and to measure their exact masses ✓
- Measuring molecular mass of a sample

So it has versatility as you can see, it gives a host of informations and I have listed only few of them in the slide. First and foremost, it allows us to determine the chemical and structural information of any molecule. Any molecule or any ionic species, you see it gives us an understanding of chemical and structural nature of that molecule. Then it allows us to identify the unknown compounds, start with.

It also allows us to quantify the known compounds. We can also determine the relative abundance of isotopes and measure the exact masses. Remember it is possible to measure the exact masses of the isotopes. Those masses you see in the books reported are basically measured using SIMS, and then it also allows us to measure the molecular mass of any sample. Correct.

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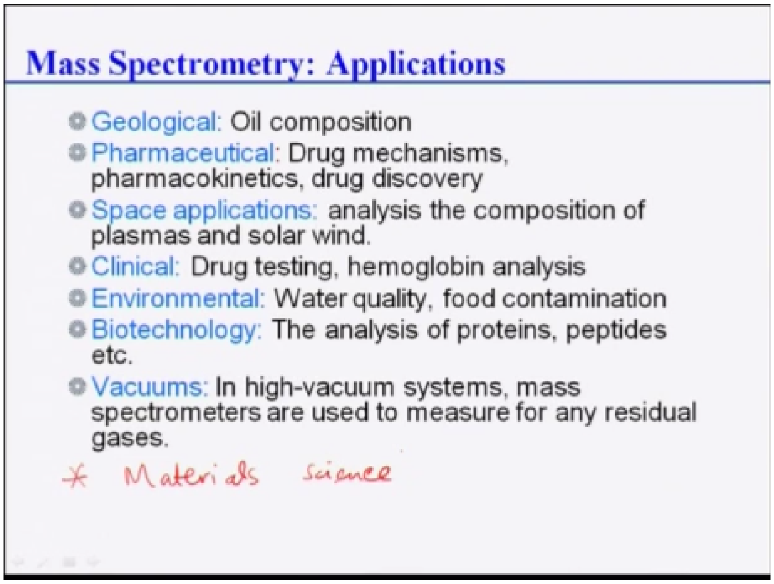

Mass Spectrometry: Applications

- Geological: Oil composition
- Pharmaceutical: Drug mechanisms, pharmacokinetics, drug discovery
- Space applications: analysis the composition of plasmas and solar wind.
- Clinical: Drug testing, hemoglobin analysis
- Environmental: Water quality, food contamination
- Biotechnology: The analysis of proteins, peptides etc.
- Vacuums: In high-vacuum systems, mass spectrometers are used to measure for any residual gases.

* Materials Science

Now if we look at the uses, it is used in wide spectrum irrespective of different branches of Science Engineering. Most important one, it is used in geological problems basically in oil consumptions or oil production units like, you know in oil production unit there are different kinds of chemical species is available, organic and it allows us to detect them. Then comes the pharmaceutical industry that is pharmocokinetics, drug discovery, drug mechanisms.

Next one which uses this technique extensively is space application like composition of the plasmas and the solar winds by the astro physicists. Obviously it can be used for environmental technique like water quality, food contamination, biotechnology, in fact it can be used in high vacuum systems, mass spectrometers to wish to measure even this fuel gases present in the particular systems.

If you look at this series, I have not mentioned about materials science. So obviously materials science is involved in all these things. We cannot use this particular spectroscopic simple technique for analyzing our day-to-day materials or the materials which you are actually preparing in the labs in detailed manner. Well, so basically after knowing this mass spectroscopy and the advantage and these things, what actually a mass spectrometer needs to have? What are the basic things it must have?

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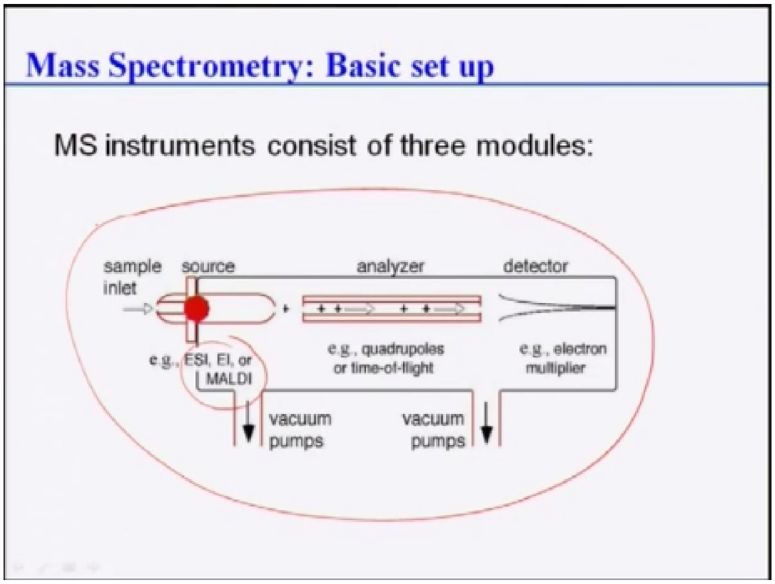

Mass Spectrometry: Basic set up

MS instruments consist of three modules:

Well basically it must obviously have a sample because that is what we are analyzing, and then we have to have outsourced of ions. So sample is ionized and we create different sources of ions. This is what is done by these techniques which I am going to discuss. And then these ions are actually analyzed based on mass to charge ratio by using either Quadrupoles or tyro flight measurements, and then they are detected either a photographic plate or electro multiplier of faraday cup a different kinds of detectors are available.

And the whole thing is has to evacuated because the ions needs to move forward on the source to detector. So their movements should not be hindered by any kind of residual molecule, gaseous molecule present in a system. So vacuum systems to be of the order of create a vacuum of that in the - 9 x - 10 power inside the chamber and these all actually leads to the cost of the instrument. So this is the basically three modules of any mass spectroscopy.

And since both the analyzer and detector remain same, all the thing which gets changed is the source. We do create secondary ions using the primary ions. But in a mass spectroscopy we use primary ions to analyze these masses. So in a natural if I have to show you in a very chart, what we need is to create ions and this can be done by ionizations.

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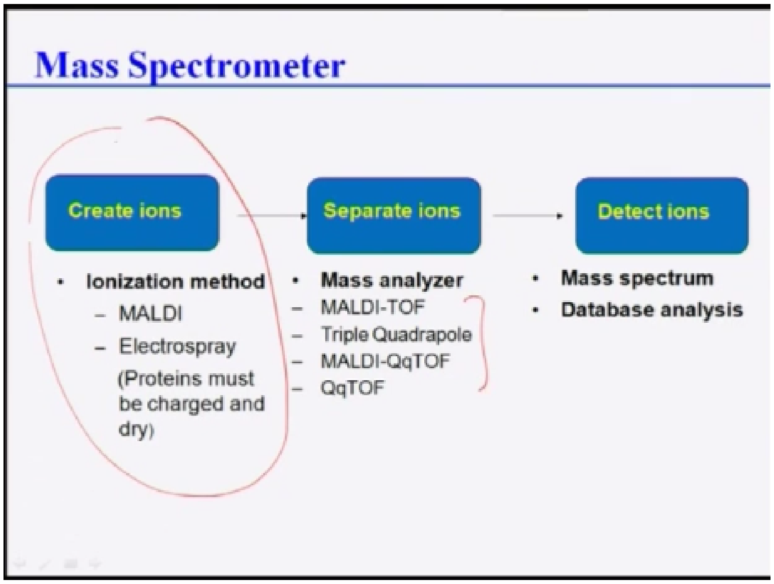

Mass Spectrometer

Create ions
- **Ionization method**
  - MALDI
  - Electrospray
    (Proteins must be charged and dry)

Separate ions
- **Mass analyzer**
  - MALDI-TOF
  - Triple Quadrapole
  - MALDI-QqTOF
  - QqTOF

Detect ions
- **Mass spectrum**
- **Database analysis**

You can do by electro spray, you can do MALDI, I will tell you. You can do even other ionization techniques like, you can use a primary source of ion and spotter and create ions, and then after you created the ions, you have to collect the ions. You collect the ions and then you separate them in different mass to charge ratio. That is what is done by mass analyzer. It can be MALDI time of flight, or it can be Quadrupole time of flight only, or it can be triple Quadrupole also.

And there are many other sections but these are the main ones. After that, we have to detect the masses and that it done by mass spectrum analysis. Also we need to have a database like X-ray diffraction, hash database and many others. So this is the main thing about mass spectroscopy. All the thing as I said was going to change in same size basically this part. The other two parts will remain same.

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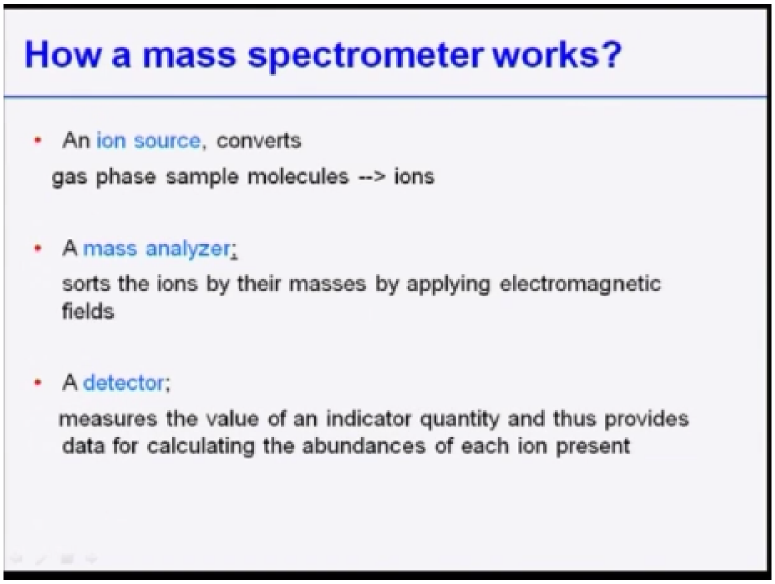

How a mass spectrometer works?

- An ion source, converts
  gas phase sample molecules --> ions
- A mass analyzer;
  sorts the ions by their masses by applying electromagnetic fields
- A detector;
  measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present

So actually you create ion source, you can have a gas ion, mass analyzer and detector. This is I have told.

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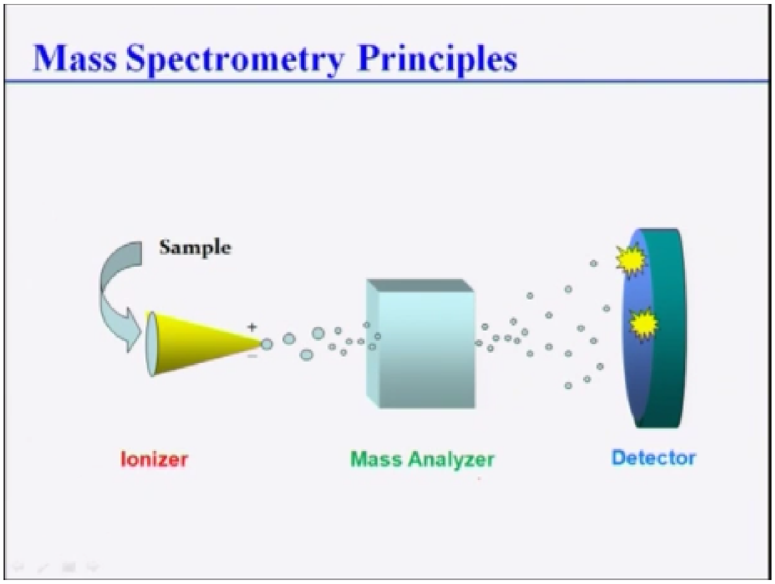
Mass Spectrometry Principles

So in a basically pictorical things, I can say there is ionizer, and there is a mass analyzer, there is a detector. That is how the ion section will move through this.

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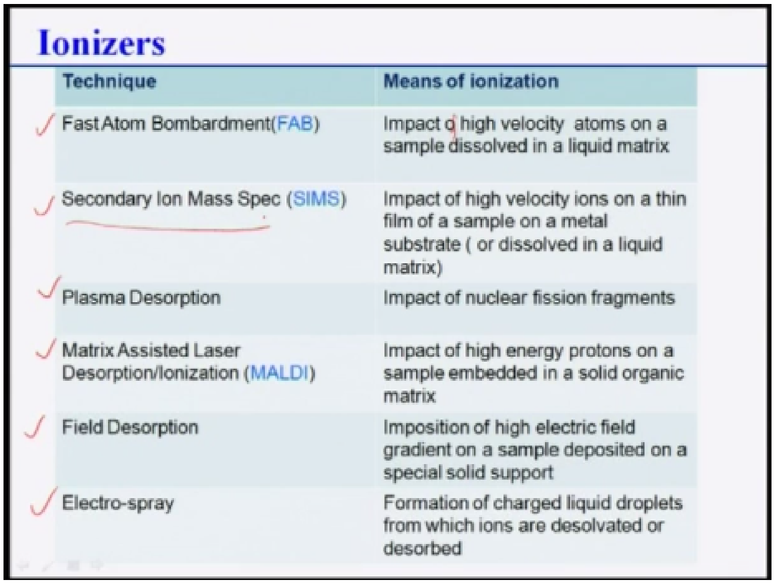

Ionizers

Technique	Means of ionization
✓ Fast Atom Bombardment(FAB)	Impact of high velocity atoms on a sample dissolved in a liquid matrix
✓ Secondary Ion Mass Spec (SIMS)	Impact of high velocity ions on a thin film of a sample on a metal substrate (or dissolved in a liquid matrix)
✓ Plasma Desorption	Impact of nuclear fission fragments
✓ Matrix Assisted Laser Desorption/Ionization (MALDI)	Impact of high energy protons on a sample embedded in a solid organic matrix
✓ Field Desorption	Imposition of high electric field gradient on a sample deposited on a special solid support
✓ Electro-spray	Formation of charged liquid droplets from which ions are desolvated or desorbed

How to ionize actually? That is what we must know. There are different ways of ionizing. First one is known as fast atomic bombardment or FAB. This is nothing but impact of high velocity atoms on a sample is also a liquid matrix. If you have a high velocity atoms like argon, or oxygen, or cesium, and these atoms actually are allowed to call on a sample which is kept inside liquid matrix, it can create ions of the atoms in a sample.

Second one is secondary ion mass spectroscopy and this is the topic of today's discussion. It is nothing but impact of high velocity ions on a thin film of a sample on a metal substrate. It can be also dissolved by liquid matrix. So by this way, these fast ion atom bombardment and secondary ion mass specs, actually the preparation of ions are almost similar. What you need to have is impact of the high velocity ions in case of SIMS and in case of fast or FAB unit of impact of high velocity atoms.

Then you can always have a plasma desorption's, this is nothing but impact of nuclear fission fragments. Nuclear fission fragments are always like alpha particle, gamma particle, beta particles. This fission fragments can lead to plasma desorption. You can also have a technique known as, so we also have discussed this, this, this we can have a technique known as Matrix Assisted Laser Desorption/Ionization which is known as MALDI, that is what I talked in the last slide.

So it thus actually creates ions by impact of high energy protons on a sample embedded in a solid organic matrix. So you create a proton, proton is nothing but Hѵ, Laser has lot of proton or quanta, and this is basically allowed to fall at a high velocity on a sample which is embedded in a solid organic matrix and that is how you can analyze ions. Then one can do field desorption on electro spray.

Field desorption is nothing but imposition of high electrical fill gradient on a sample deposited on a special solid support. Those of you who have some idea about atom probe; in atom probe we do the same thing actually. We have created large, we impose a high electrical field between the sample and the electrode, and because of the creation of the high electric field, the ions on the sample is just dislarged or the atoms of sample are dislarged and created comprises a ion.

Electro spray is basically is very simple, simple of all these techniques. It is nothing but formation of charged liquid droplets from which ions are desolvated or dissolved. If you have a charged liquid droplet, you can create the liquid droplets by using electrical field or the spray using electrical field and then you can dissolve it or desorb. So these are the different techniques of ionizations which is done.

So you see, SIMS comes as one of the techniques of ionizations, not all since there are many other techniques. So that is why I want to discuss mass spectroscopy in togetherness. Now how do you then after getting the ions, you have to analyze the masses. How to analyze the masses? There are host of techniques available. That is what the discovery is happen. First and very simple one is single focusing magnetic deflection which I will tell you.

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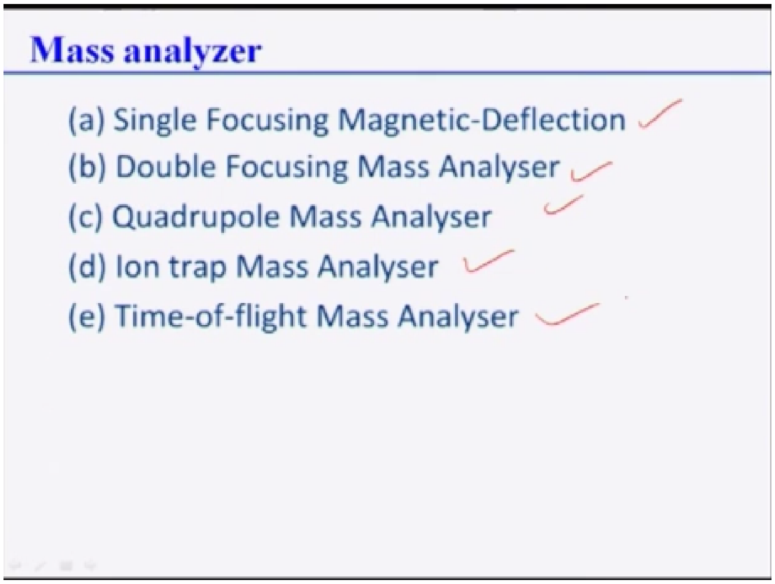

Mass analyzer

(a) Single Focusing Magnetic-Deflection ✓
(b) Double Focusing Mass Analyser ✓
(c) Quadrupole Mass Analyser ✓
(d) Ion trap Mass Analyser ✓
(e) Time-of-flight Mass Analyser ✓

Second one is double focusing magnetic analyzer. Third one which is wildly used is Quadrupole mass analyzer. Then you have mass analyzer and then the last one, which is very popular one is known as Time of Flight mass analyzer.

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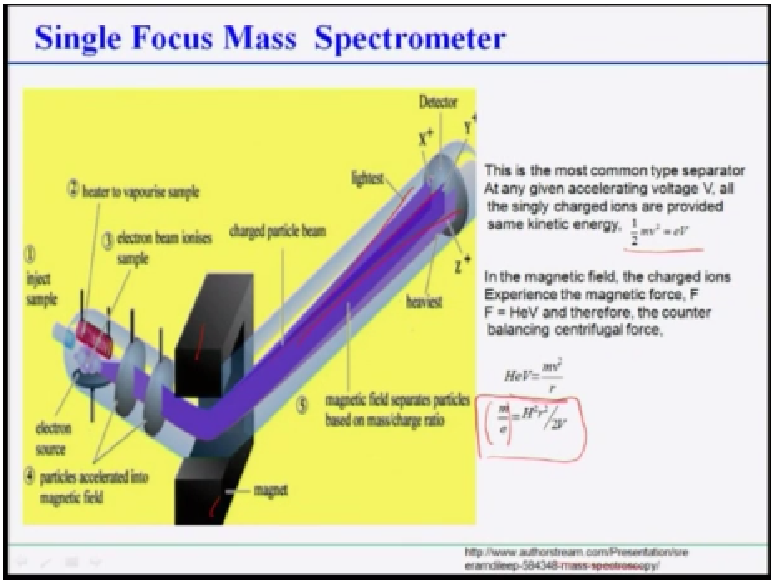

Single Focus Mass Spectrometer

This is the most common type separator
At any given accelerating voltage V, all the singly charged ions are provided same kinetic energy, $\frac{1}{2}mv^2 = eV$

In the magnetic field, the charged ions Experience the magnetic force, F
F = HeV and therefore, the counter balancing centrifugal force,

$$HeV = \frac{mv^2}{r}$$

$$\boxed{\left(\frac{m}{e}\right) = H^2r^2/2V}$$

http://www.authorstream.com/Presentation/sreeramdileep-584348-mass-spectroscopy/

Let us look at them. This particular slide is on single focus mass spectrometer and this is a very simple technique. This picture schematic is taken from this one, there is a presentation available on the website. What is done here? Let me first explain the theory. This is the most common type separator. At any given accelerating voltage V suppose, all the single charged ions has provided some kinetic energy, and that is given by this electronic charge E multiplied by the accelerating voltage v must be equal to kinetic energy of the charged species, that is ½ mv^2.

Now if you allow this charged accelerated species to pass through a magnetic field which is shown here. This is the magnet you see. The charge and so you will experience a magnetic force, and this magnetic force is given by HeV, where H is the magnetic field strength. So therefore this is balanced, this magnetic force is balanced by the centrifugal force obviously. So that means you can write down HeV must be equal to centrifugal force that is Mv^2/r.

So you get $m/e = a^2\ r^2/2V$ straight forward and this is what is the classical equation which allows us to separate different species with different values of m/e ratio. As you can see, depending on the different m/e ratio, if you keep H and P constant, R will change. So therefore, lighter ones will come as a smaller r and heavier ones come as a very larger r. So that is how actually you can differentiate between different charged species with different m/e ratios.

It is very simple actually in fact with first you charge and accelerate, and then as soon as it has charged and passed through the magnetic field and it separates out. That is how it is done. So we are focusing with single magnets. That is why it is called a single focus mass spectrometer.

Remember this is actually how we can actually separate the ions very easily and subsequently what all techniques, separate techniques we will see; they are actually modification of this one.

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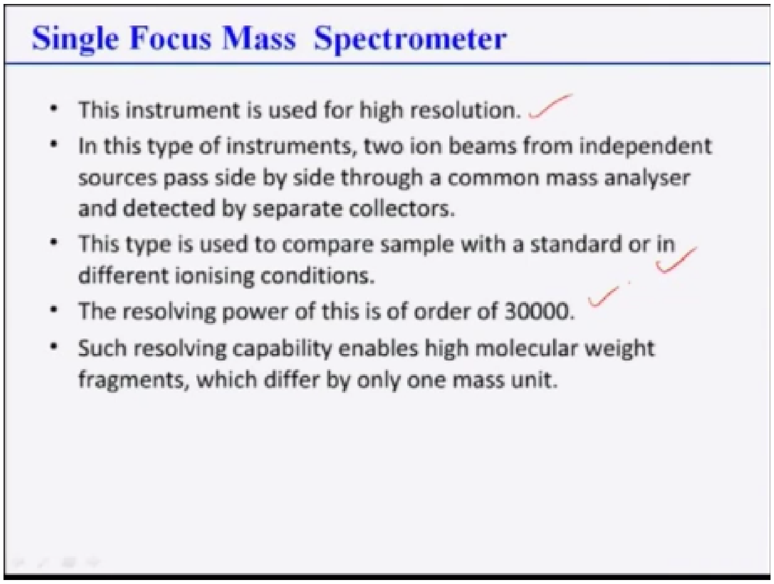

Single Focus Mass Spectrometer

- This instrument is used for high resolution. ✓
- In this type of instruments, two ion beams from independent sources pass side by side through a common mass analyser and detected by separate collectors.
- This type is used to compare sample with a standard or in different ionising conditions. ✓
- The resolving power of this is of order of 30000. ✓
- Such resolving capability enables high molecular weight fragments, which differ by only one mass unit.

So it very high resolution this instrument gives actually. This gives you wide substance in the high resolutions in the sense of PPL level detection possible. In this type of instrument, two ion beams form independent sources passes side by side through a common mass analyzer and detected by separate collectors. This is used to compare sample of the standard or through different ionizing condition. The resultant power is order of 30,000.

Such resolving capability enables high molecular weight fragments which differ only by one mass unit. That means if there are two species with a mass only difference of 30,000 and 29,999 still you can detect by this that is what the resolution of this instrument.

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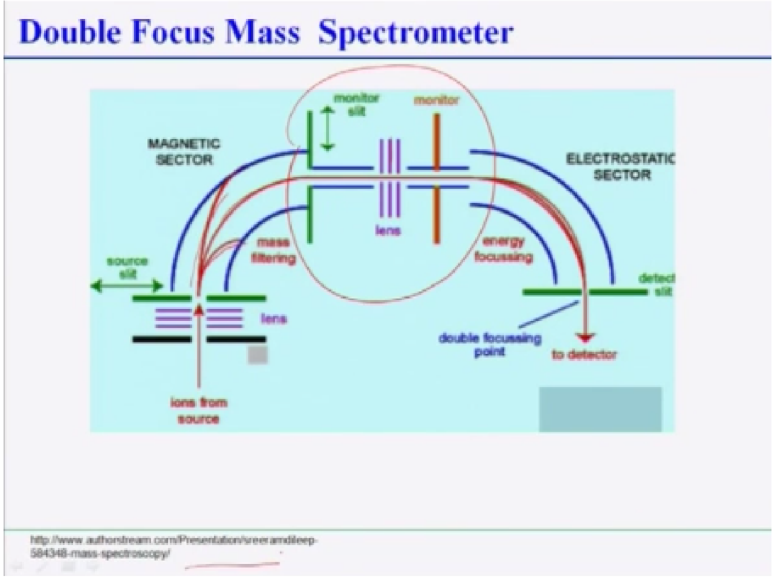

Double Focus Mass Spectrometer

http://www.authorstream.com/Presentation/sreeramdileep-584348-mass-spectroscopy/

Next one which is also widely used quite some time is known as double focus mass spectrometer. What is double focus mass spectrometer? Well, single focus mass spectrometer, you have seen here we are using two focusing magnets. So you have, you can see this is the lens and then basically ion sources come through this. This is the ion source, and then it passes through a lens.

There is a source slit and then there is a magnetic field, it just basically magnetic sector it just separate this ions out or filters the masses, and then it passes through this single mass whichever is basically passing through this radius which is matching with the slit will pass through a top of the detector. So if you change the slit little bit or if you change the magnetic movement, that is H value, you can allow either this one or this one or this one to pass through this slit and the detector.

That is the advantage as compared to the first technique, a single focus mass spectrometer. It has very much better resolution than the single focus mass spectrometer. That is mainly because there is extra attachment like this possible have. That is why it is called a double focus, because first you are focusing this magnetic sector, then you are focusing with the electrostatic sector and that is how actually you can detect very precisely each and every charged species. This is again taken from one of the websites which is available on the internet.

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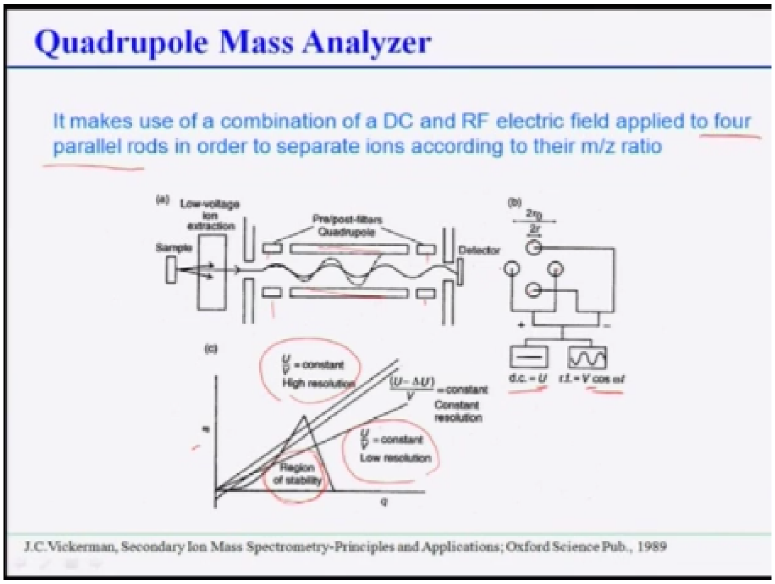

Quadrupole Mass Analyzer

It makes use of a combination of a DC and RF electric field applied to four parallel rods in order to separate ions according to their m/z ratio

J.C.Vickerman, Secondary Ion Mass Spectrometry-Principles and Applications; Oxford Science Pub., 1989

Next one and probably one of the best one is Quadrupole mass analyzer. The reason I am saying this is the best one, because it allows ours, even better measurement than a single focus or double focus magnetic spectrometer. Well it makes use of with combination of direct current and rare frequency electric field applied to four parallel rods remember it is applied to four parallel rods to separate the ions acting to their mass by charge ratio.

So we are using direct current as well as rare frequency electric field and using four parallel rods, that is why it is called Quadrupole, to separate the ions. What is done here? It is taken from Vickerman's book. So I have a sample, you create ions by different ionization techniques and then you have 1, 2 these are actually filters, post or pre filters Quadrupole. They are the four important ones, and then it passes through this region where this Quadrupole actually separates the ions depending on its mass to charge ratio and detected.

You can see here, this is a DC voltage, this is the RF voltage. You can apply and repeat these are the four probes or different dimensions. Now if I plot the movement of the ions, you can see here, these are the two parameters A and Q, Q is the charge, and A is basically the distance between the Quadrupoles. So if you can see the plots you see here, there are different regions. This is U/V constant and low resolution, U/V constant high resolution, U and V. This is U-ΔU/V constant but constant resolutions, and this is, what is the region of stability?

So that means we can change U and V in such a way, U is basically DC voltage, and V is the RF voltage magnitude. So by playing around these two we can actually get into this region of stability and that is the region one which you need to worry. Obviously if I want to work with U and V because of high resolution, you can do that or you can want to work with constant you can do that depending on the systems on which you are working on. So as you see this gives us many, many possibilities of changing the conditions and do the measurements.

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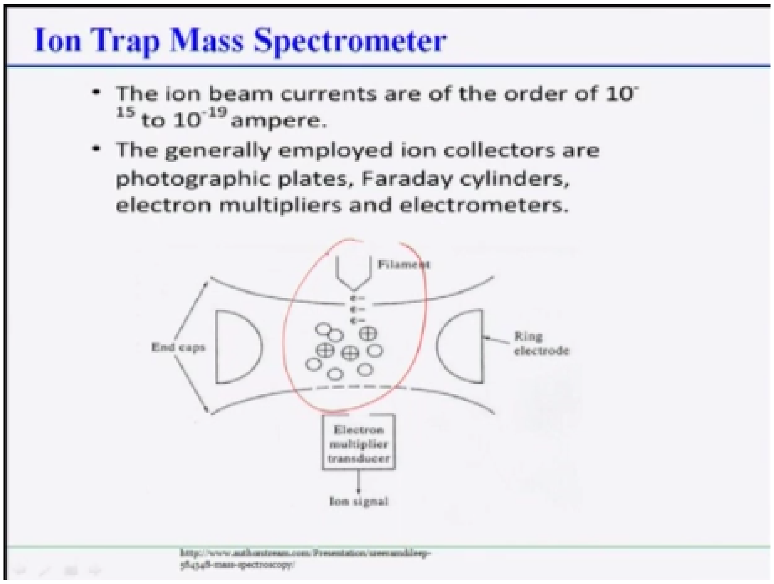

Ion Trap Mass Spectrometer

- The ion beam currents are of the order of 10^{-15} to 10^{-19} ampere.
- The generally employed ion collectors are photographic plates, Faraday cylinders, electron multipliers and electrometers.

Fourth technique which is important is ion trap mass spectrometer. As the name suggests, it is basically traps as you know Paul actually got Nobel Prize, because of iron trap technique availability. I have told you that in 1983. Ion beam currents are normally of the order of 10^{-15} to 10^{-19} amperes. It is very small that is because the number of ions present in the source beam is very small.

This thing which I already employed ion collectors and they are actually photographic plates, or electron multipliers. So what is done here? You have basically filament and which actually creates ions or charged species, and then we have these kind of ring electrodes which basically collects or traps these ions and after that we can actually use this mass spectroscopy, this kind of single focus or double focus or Quadrupole, and then we can actually analyze these mass by charge ratio.

And finally we can detect them using transducer that is why you will get. So basically preparation wise distinctly defines from the other three techniques. This is normally not used much except for few specific applications. This one is also taken from this website.

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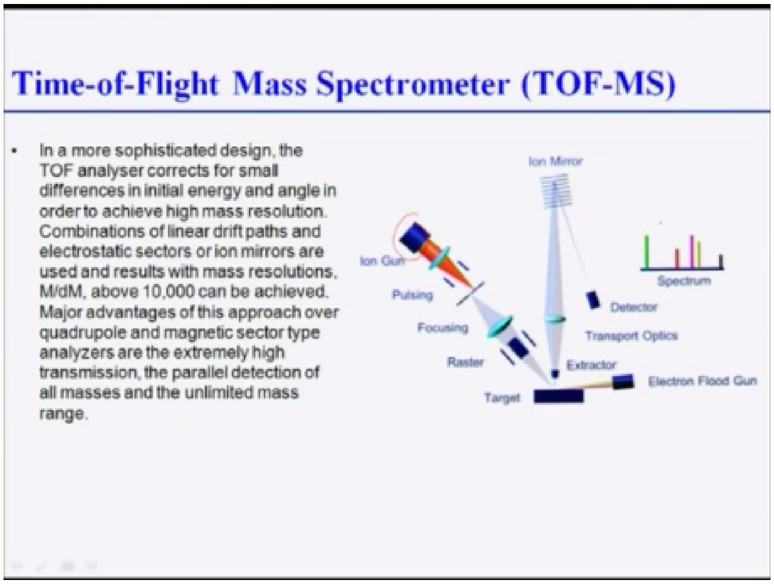

Time-of-Flight Mass Spectrometer (TOF-MS)

- In a more sophisticated design, the TOF analyser corrects for small differences in initial energy and angle in order to achieve high mass resolution. Combinations of linear drift paths and electrostatic sectors or ion mirrors are used and results with mass resolutions, M/dM, above 10,000 can be achieved. Major advantages of this approach over quadrupole and magnetic sector type analyzers are the extremely high transmission, the parallel detection of all masses and the unlimited mass range.

Well the last technique which I am talking about is what is known as Time of Flight Mass Spectrometer. A schematic source per technique actually. What is here, you look at it very carefully. You have a ion gun which ionizes the species and then there is a pulsing action, it can pulse actually. Hand gun can obviously pulse like laser beam, and then you can focus this. It also allows the hand gun allows to raster like ion guns.

And then once it falls on the target, it creates ions for the circle surface, and then it passes through this extractor which extract the ions which is coming because of this ionization due to ion gun. That means we are creating a secondary ions actually, and then basically ion mirrors which is nothing but Quadrupole detector or maybe a time applied detector. It basically separates the ion and detects and it takes and gives you the spectrum. Correct.

So many cases as you create more ions, so you have to have electron flat gun, otherwise charge balance will not be in the sample surface. In a more sophisticated design, the time of flight analyzes, corrects for the small differences in initial energy and angle inward to achieve high mass resolutions. It is a combination of linear drift paths electrostatic sectors or the ion mirrors which are used and results are comes with the mass resolutions of above 10,000 can be achieved.

Advantage of this technique about the Quadrupole and the magnetic sector type is that extremely high transmission, parallel detection of all masses and unlimited mass range is possible. Yes, because it does not use, because what we are doing is basically time of flight measurements. How much time a mass takes to fly or move in a particular distance and depending on that you can differentiate it among different species. We are not using the exactly m/z ratio. So let me just give you the Mathematics of it.

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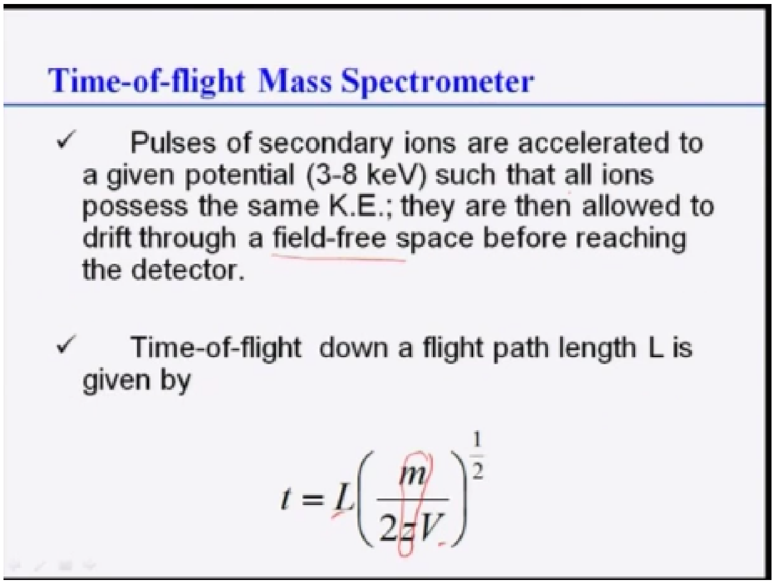

Time-of-flight Mass Spectrometer

- ✓ Pulses of secondary ions are accelerated to a given potential (3-8 keV) such that all ions possess the same K.E.; they are then allowed to drift through a field-free space before reaching the detector.
- ✓ Time-of-flight down a flight path length L is given by

$$t = L\left(\frac{m}{2zV}\right)^{\frac{1}{2}}$$

Pulses of secondary ions are accelerated as you know ion gun create secondary ions, and pulses of secondary ions are accelerated to give a potential which is of the order of certain keV 3-8 such that all the ions possesses same kinetic energies. Then these ions allowed to drift their field's free space. Remember after these ions are accelerated passing the ions, they are allowed to pass through a drift, through a field's free space. We are not applying any magnetic electrostatic field before using a detector.

And when it passes through because they have the same kinetic energy m/mv^2, but whereas it will be different. So because of this, masses are different, velocities will be different, because of this the time it takes to move a length will be given by $L(m/2zv)^{1/2}$, L is basically the flight path length, M is the mass, Z is the ionic charge, and V is the accelerating voltage. So as you can see depending on m/z values, if for even L and V are constant, T will be differed.

And by knowing the different times, we can actually separate these ions very easily. This is actually widely used now what the worldwide technique and it has many advantages. Now if I go back to the previous slide that is what is done. In the ion mirror within the extractor and ion beam what is done is that this secondary ions having same kinetic energy travels at drifts to a path of certain lengths, lengths may be this much and get separated out. And then we can plot, I will show you the plots also later; we can plot and get idea of that.

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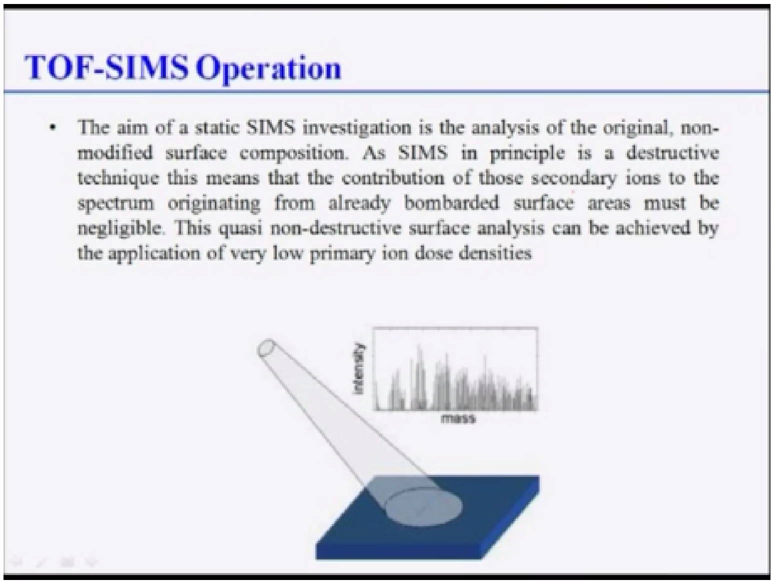

TOF-SIMS Operation

- The aim of a static SIMS investigation is the analysis of the original, non-modified surface composition. As SIMS in principle is a destructive technique this means that the contribution of those secondary ions to the spectrum originating from already bombarded surface areas must be negligible. This quasi non-destructive surface analysis can be achieved by the application of very low primary ion dose densities

So this is I am going to discuss in detail when I come to SIMS, so but to give you some idea in a static SIM experiments, it actually analyzes the original, non-modified surface compositions, uses time of flight measurements. And it basically is a quasi non-destructive surface analysis because it uses very low dose.

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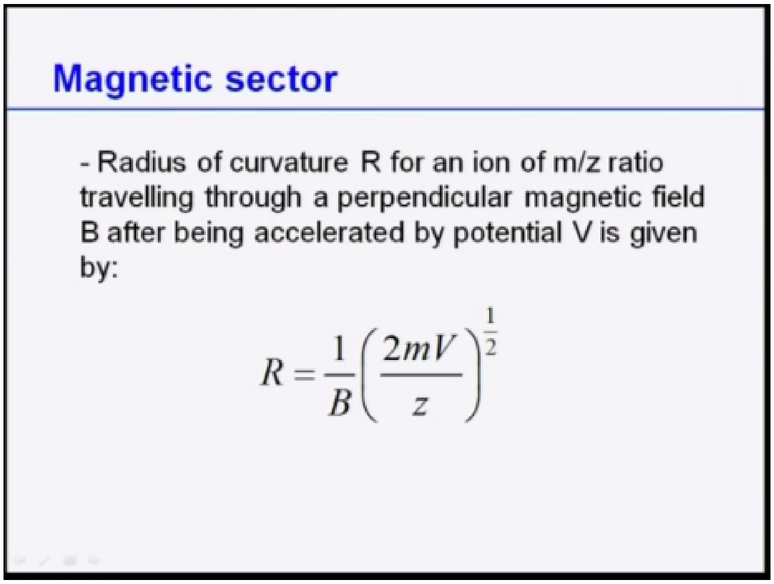

Magnetic sector

- Radius of curvature R for an ion of m/z ratio travelling through a perpendicular magnetic field B after being accelerated by potential V is given by:

$$R = \frac{1}{B}\left(\frac{2mV}{z}\right)^{\frac{1}{2}}$$

Well as I have talked about lot of different magnetic focus like single magnetic focus or double magnetic focus or even Quadrupole, let me just give you some idea about what a radius of curvature means? How does the ions easily get curved? Radius of curvature of any ions of distinct m/z ratio travelling through a perpendicular magnetic field B, after it has been accelerated by a certain potential is nothing but $1/B(2mV/z)^{1/2}$.

So if B is constant, P is constant, it depends on the m/z. So ions actually travelling as I go back at different radius that will depend on m/v. So that is what actually used in this technique.

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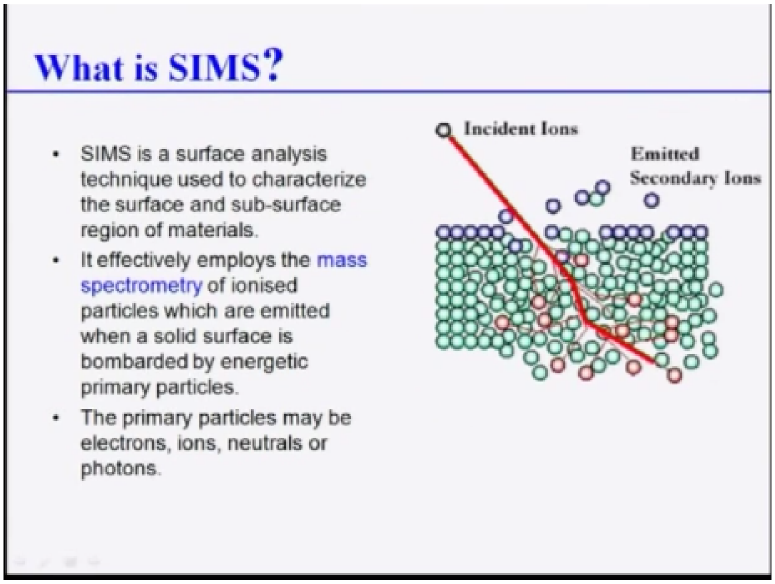

What is SIMS?

- SIMS is a surface analysis technique used to characterize the surface and sub-surface region of materials.
- It effectively employs the mass spectrometry of ionised particles which are emitted when a solid surface is bombarded by energetic primary particles.
- The primary particles may be electrons, ions, neutrals or photons.

Now after giving huge introduction, lot of things I have talked about it, about the mass spectroscopy. Let me just get into details of the secondary ion mass spectroscopy. Although there are many things which are similar, but distinct things, the things which are distinct and since as compared to this MS or mass spectroscopy is to be known to you very clearly. SIMS per se is a surface analysis technique.

Remember this. Mass spectroscopy may not be substances technique. SIMS is specifically a surface analysis technique. It is used to characterize surface and soft surface regions of any material. Thus actually what makes SIMS very popular, because if you have a thin film in the surface of any material, you can analyze it to the position of SIMS, it can give you PPM level position?

It effectively employs this mass spectrometry what I discussed of ionized particles which are imitate when a solid surface is bombarded by energetic particles. The schematic diagram on the right side up to you is showing this picture. We have a incident ion source. It can be ion which I'm going to discuss any ion, in fact this is what is one of the things which I will discuss. Instead ions which can be either cesium ion, or it can be oxygen ion or it can be other ions, but mostly cesium and oxygen ions are used which are actually accelerated with certain kinetic energies.

And then they allow to fall on the surface of a sample or a target and once it comes, it creates a cascade of events in which imitate secondary ions from the samples or imitate. So primary particles are mostly ions or either it can be protons also, or it can be neutral species also, and it can be chart species also, but they are actually primary ions and they are actually the samples surface and create the ions.

If I have to tell you about that in a secondary I have SIMS, the primary ion sources are created by instrument by Duoplasmatron. It is the one which can create different ions, and it can actually use, it can create ions like different gases, oxygen is basically commonly used in the SIMS, oxygen can comes as a O- or O2+or it can comes even O2-. Who has surprise what are these?

O- is basically when all the oxygen are stripped, O2+ is that the one oxygen is stripped and O2- one extra electron is added. So that means we can have positively charged ion and negatively charged ion and also heavily charged ion, O2- and O-. So we can create all kinds of chart species, and then these primary ions are allowed to fall on the sample surface to create this. So, O- is the most abandoned species used while polyatomic ions are also used.

If we have insulating material, then we have to use O- ion, because otherwise there will be charged spilled over the surface. And the second type of SIMS also uses something known as caecilian ion. It is to enhance actually yield of this electronegative elements like carbon, oxygen, or even sulfur, but there are very low atomic mass elements, we use CS+ ion, cesium ion actually operate in the positive morns to create CS+ ions.

Generally CS+ are smaller, and then generated by Duoplasmatron, duoplasmatron create oxygen ions basically, it can create others but mostly, and so far the CS ions are basically much final and it can sputtering basically this is taken a sputtering process yet bringing in primary hands and sputtering. Again sputtering actually more material effectively, because of their greater mass, and it is normally used to extensively measure the different isotopes, and when you using insulating material, you can always use CS+ ions.

As you know, the most of these things that surface analyzing process so there it lead to hitting out this samples and sometimes, it can create other problems also. So, let me give little bit idea about what is the collusion, how does the collusion happens.

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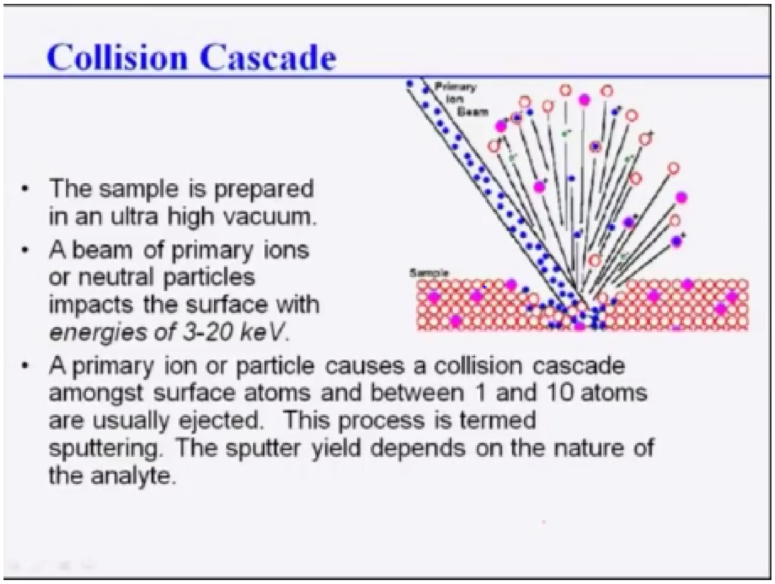

Collision Cascade

- The sample is prepared in an ultra high vacuum.
- A beam of primary ions or neutral particles impacts the surface with *energies of 3-20 keV*.
- A primary ion or particle causes a collision cascade amongst surface atoms and between 1 and 10 atoms are usually ejected. This process is termed sputtering. The sputter yield depends on the nature of the analyte.

This is nothing but a collusions cascade, a sample is prepared in a vacuum, and then put a primary hands of this much energy, 3 to 20 kilovolts. It causes a collusion cascade among the surface atoms and between 1 and 10 is where actually ions are created. This is always just sputtering but sputtering by using primary hands. Sputtering will depends on the nature of the sample also.

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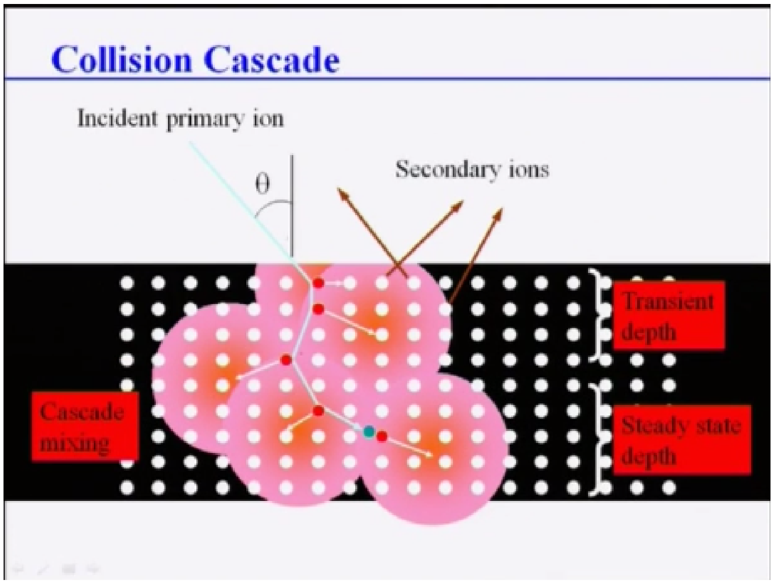

Collision Cascade

Now what is collision cascade? If an incident primary being termite at the angle θ with respect to surface normal this can create large you can see, number of secondary ions. So one can create other, other can create another one, and then goes on that is what is called cascade collision cascade and this leads to cascade mixing in the sample, so initial depths will be transient one, and then finally when the cascade is stabilized these kind of origin of the surface ions is called steady state steps.

So therefore, measurements from the steady state steps are surely much better than the transient one. So we have discussed about collision cascade in an interaction of primary ions with the sample surface.

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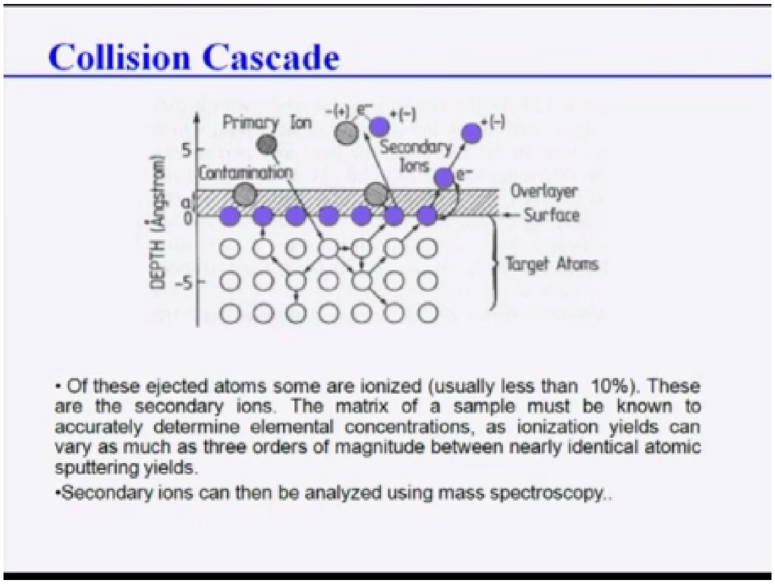

Collision Cascade

- Of these ejected atoms some are ionized (usually less than 10%). These are the secondary ions. The matrix of a sample must be known to accurately determine elemental concentrations, as ionization yields can vary as much as three orders of magnitude between nearly identical atomic sputtering yields.
- Secondary ions can then be analyzed using mass spectroscopy..

To give you a better idea of that I am just showing you this schematic picture, this one is showing you the atoms and the primary and the secondary ions. As you see, the primary different atoms in the samples are appears which is shown here like this and these are known as target atoms, these one which I marked. And then we have a surface atom which have marked in blue, and you will always have layer which contains contamination.

So primary ions which are coming at very high energy, the carbons hits suppose this is a primary and comes in this atom and this atom is rejected or moved. This atom has so many choices, it can either go and hit this, or this, or this one, and subsequently those atoms which are hit can also hit other atoms and thus this cascade is created, and finally it uses surface atom and secondary ion comes into picture and these are all secondary ion and that one they are. So of these ejected atoms from NH usually less than 10% and these are all called secondary ions.

The matrix of the samples must be known to accurately determine the elemental concentration as ionization yields can vary very much as much as order three orders matching between nearly identical atoms sputtering yields. Secondary ions can then be analyzed using mass spectroscopy which I have discussed.

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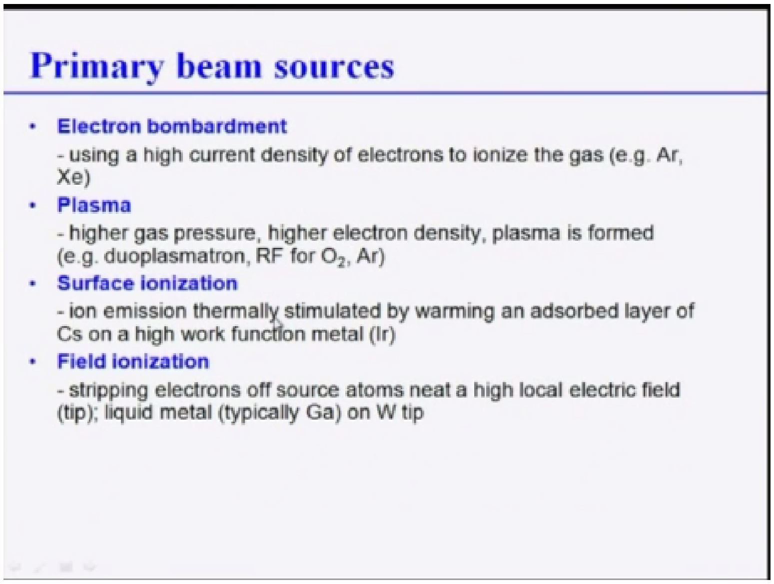

Primary beam sources

- **Electron bombardment**
  - using a high current density of electrons to ionize the gas (e.g. Ar, Xe)
- **Plasma**
  - higher gas pressure, higher electron density, plasma is formed (e.g. duoplasmatron, RF for O_2, Ar)
- **Surface ionization**
  - ion emission thermally stimulated by warming an adsorbed layer of Cs on a high work function metal (Ir)
- **Field ionization**
  - stripping electrons off source atoms neat a high local electric field (tip); liquid metal (typically Ga) on W tip

Now there are many ion sourcing SIMS, they are most widely used as I discussed is oxygen and cesium, but one can use also electron as an ion source, you can have high current and set of electrons like to analyze basically argon or xenon, you can always use plasma. Plasma is nothing but ionic charge gas, it is a high pressure, high electron density and plasma is normally is formed in duoplasmatron which I discussed, you always have air frequency for oxygen argon.

You can also have something know as surface ionization. Ion emission is primarily simulated by warning and absorbed layer of cesium on a high working metal like iridium; you can do that because the thermal simulation can always lead to surface ionization. Easiest but the best one is the fill emission, fill ionization, you can strip off electrons from the source atoms very neatly by using a high local electric field.

For that you need a very fine tip and this is what done in atom probe or we are going to have a liquid metal, typically gallium on tungsten tip. So, any of these things can be used and also you can use cesium and oxygen as I said.

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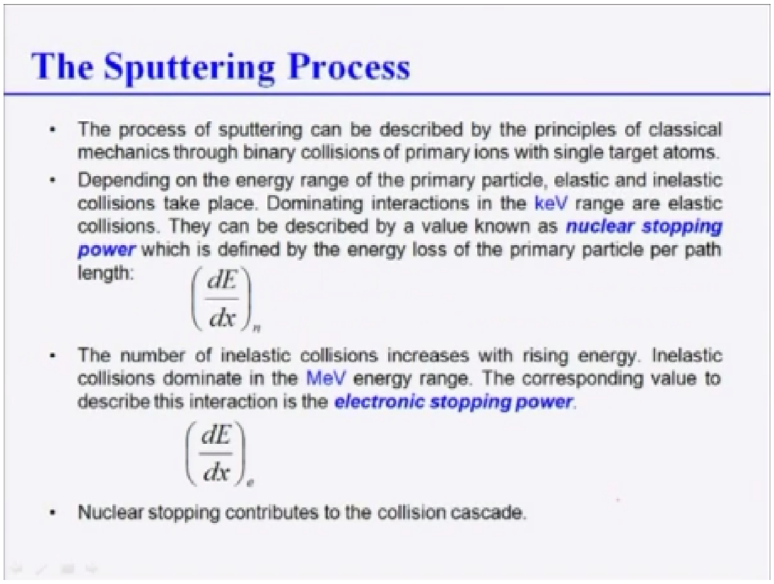

The Sputtering Process

- The process of sputtering can be described by the principles of classical mechanics through binary collisions of primary ions with single target atoms.
- Depending on the energy range of the primary particle, elastic and inelastic collisions take place. Dominating interactions in the keV range are elastic collisions. They can be described by a value known as ***nuclear stopping power*** which is defined by the energy loss of the primary particle per path length: $\left(\frac{dE}{dx}\right)_n$
- The number of inelastic collisions increases with rising energy. Inelastic collisions dominate in the MeV energy range. The corresponding value to describe this interaction is the ***electronic stopping power***. $\left(\frac{dE}{dx}\right)_e$
- Nuclear stopping contributes to the collision cascade.

Now, what is basically the sputtering process, all this is a collusion cascade, but this basically a sputtering? The process sputtering is described with the principle of classical mechanics by binary collusions or primary ions with a single target atoms. Depending on the energy range of the primary particles or primary ions, elastic and inelastic scattering both are possible. The dominate interactions in the keV range are elastic collisions.

They can be described by a parameter which is well known as a nuclear stopping power in the literature, and this is defined as the energy loss of the primary particle per path length. So, if the primary particle is losing energy because of this sputtering process, we can always take (dE/dx) as a parameter to determine the interaction between the primary ions and secondary ions and this is what known as a nuclear stopping power.

The number of inelastic collusion increases with rising energy as usual, inelastic scattering is normally dominates if you have energies in the million electron volt. So that is why very high energy ones actually leads to lot of inelastic scattering which are not good. In those cases corresponding value to describe interaction is known as electronic stopping power and this is known as $(dE/dx)_e$.

Nuclear stopping power actually contributes to the collusion cascade; these are the two ways of basically turning this sputtering process.

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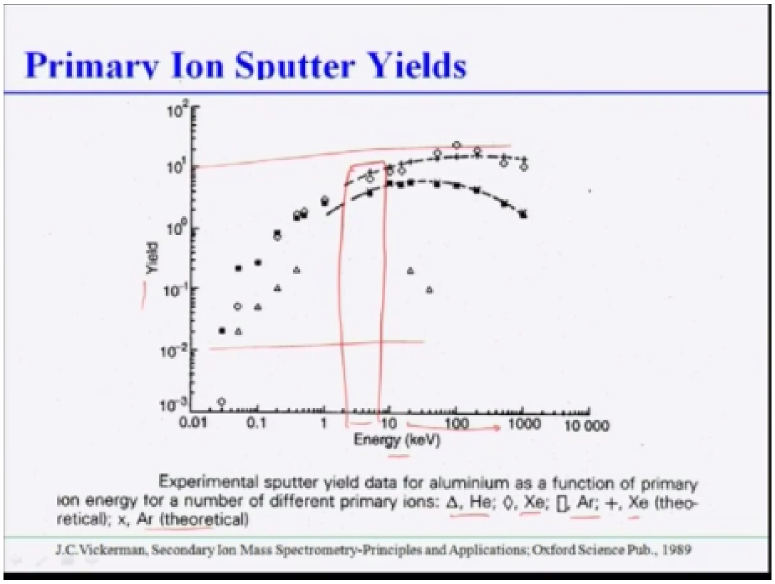

Primary Ion Sputter Yields

Experimental sputter yield data for aluminium as a function of primary ion energy for a number of different primary ions: Δ, He; ◊, Xe; ▯, Ar; +, Xe (theoretical); x, Ar (theoretical)

J.C.Vickerman, Secondary Ion Mass Spectrometry-Principles and Applications; Oxford Science Pub., 1989

Now it is also important to know that primary ion sputter yield by how many primary ions are actually, when the sputtering how many secondary ions are created per units of primary ion, this is taken from Vickerman's book. This is a plot of yield versus energy as you see yields that is -3 to +2 that means it average from very low value to 1000, and these are the different data from the helium, xenon, argon or some theoretical calculation you see here.

Sputtering will actually varies from 10^{-2} to 10^1 that is 10, it does not increase this much. Yield means basically number of secondary ion created per primary ions. So that means when it is 10 one primary ion creates 10 secondary ions, one is -2 that means to create one secondary ion you need 100 primary ions, so as you see as this energy increases sputtering yield increases. If you normally, we can use from 10 to 100, 150, 200 electron volts as the energy.

Sometimes people use C to 10 also, this is also not bad, you can see in this window also you have something like 5 to 6 secondary ions per unit, per primary ions can be created.

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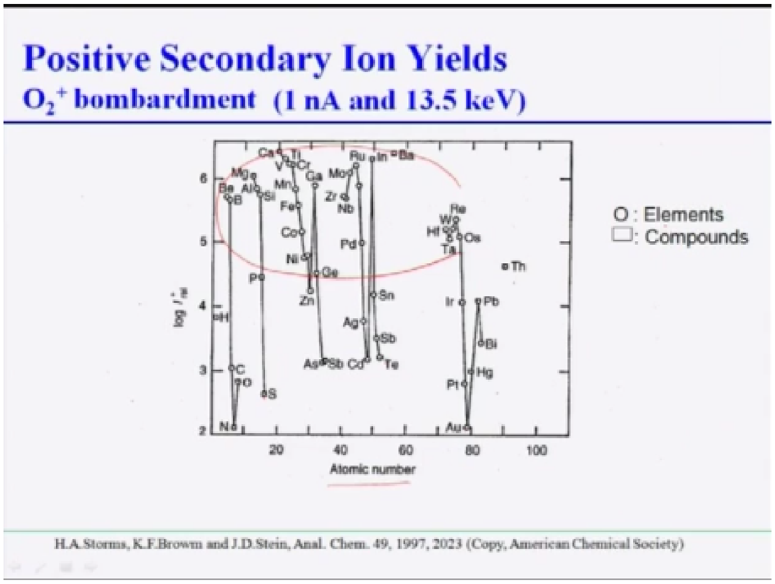

Positive Secondary Ion Yields

O_2^+ bombardment (1 nA and 13.5 keV)

O : Elements
☐: Compounds

H.A.Storms, K.F.Browm and J.D.Stein, Anal. Chem. 49, 1997, 2023 (Copy, American Chemical Society)

Well, obviously, as I said, $O2^+$, O^-, $O2^-$ ions are used. If we use that we can actually create secondary ions if this as a primary ions. So positive secondary ions yields when you have $O2^+$ bombardment is plotted here as a function of atom number. This will see for element like nitrogen, sulfa, tellurium, gold, platinum, very low lock to the power actually 3, but if you go to this one, magnesium, calcium, vanadium, manganese R and these sets is very high, I+ is 10^{45}.

So therefore, the amount of yield or amount of the secondary ions is created when you have $O2^+$ bombardment is good for this kind of elements, not for other ones.

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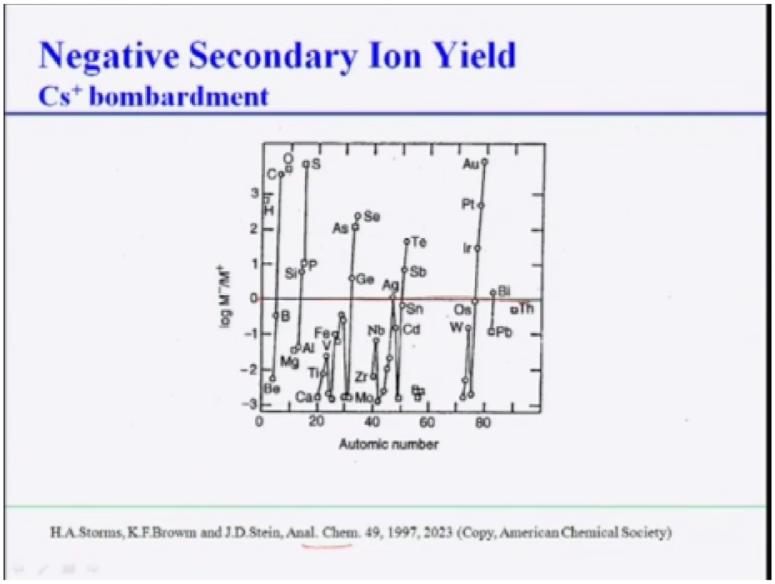

Negative Secondary Ion Yield

Cs$^+$ bombardment

H.A.Storms, K.F.Browm and J.D.Stein, Anal. Chem. 49, 1997, 2023 (Copy, American Chemical Society)

If you see a plasma bombardment, what happens, this is M- +M+ ions those are two in number, as you see here, this is taken from this paper in analytical chemistry from American society. As you see here 0 yield, 0 log0 is basically means one, so above this these are good, so those are carbon, oxygen, sulfa, silicone, phosphorous, arsenic, selenium, germanium to some extent, silver, antimony, tellurium, iridium, platinum and gold, cesium is good.

But for these metals like ion, aluminum, magnesium, zirconium, tungsten, probably oxygen 2+ ion is better, that is what is shown here. So that is why CS and O2$^+$, they can complement each other as a primary frame to create good yield of the secondary ions.

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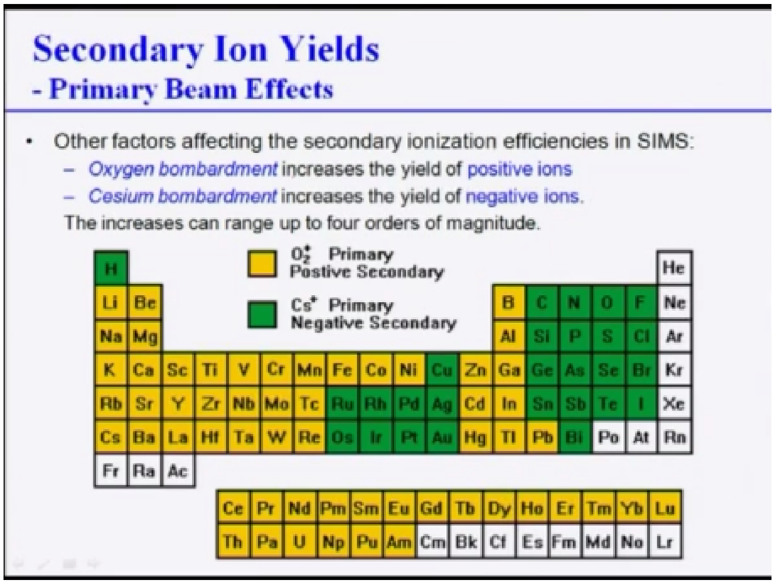

Secondary Ion Yields

- Primary Beam Effects

- Other factors affecting the secondary ionization efficiencies in SIMS:
  - *Oxygen bombardment* increases the yield of positive ions
  - *Cesium bombardment* increases the yield of negative ions.

  The increases can range up to four orders of magnitude.

🟨 O_2^+ Primary Postive Secondary

🟩 Cs^+ Primary Negative Secondary

🟩 H																	He
🟨 Li	🟨 Be											🟨 B	🟩 C	🟩 N	🟩 O	🟩 F	Ne
🟨 Na	🟨 Mg											🟨 Al	🟩 Si	🟩 P	🟩 S	🟩 Cl	Ar
🟨 K	🟨 Ca	🟨 Sc	🟨 Ti	🟨 V	🟨 Cr	🟨 Mn	🟨 Fe	🟨 Co	🟨 Ni	🟩 Cu	🟨 Zn	🟨 Ga	🟩 Ge	🟩 As	🟩 Se	🟩 Br	Kr
🟨 Rb	🟨 Sr	🟨 Y	🟨 Zr	🟨 Nb	🟨 Mo	🟨 Tc	🟩 Ru	🟩 Rh	🟩 Pd	🟩 Ag	🟨 Cd	🟨 In	🟩 Sn	🟩 Sb	🟩 Te	🟩 I	Xe
🟨 Cs	🟨 Ba	🟨 La	🟨 Hf	🟨 Ta	🟨 W	🟨 Re	🟩 Os	🟩 Ir	🟩 Pt	🟩 Au	🟨 Hg	🟨 Tl	🟨 Pb	🟩 Bi	Po	At	Rn
Fr	Ra	Ac															
			🟨 Ce	🟨 Pr	🟨 Nd	🟨 Pm	🟨 Sm	🟨 Eu	🟨 Gd	🟨 Tb	🟨 Dy	🟨 Ho	🟨 Er	🟨 Tm	🟨 Yb	🟨 Lu	
			🟨 Th	🟨 Pa	🟨 U	🟨 Np	🟨 Pu	🟨 Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

And this is what I am showing in a period table, secondary ion yields when a primary beams like that. The factor up in the secondary ions seems are oxygen bombardment, increased the yield of positive ions, cesium bombard yield of negative ions as you see. The increases can range up to four orders of magnitudes. The yellow ones are basically O2 positive secondary ions, and green ones are basically CS positive leads to ion significant relation.

As you see this one lithium, sodium, and also these sets are atoms, or these set of actually elements are good for oxygen plus positive ions to create secondary ion yields, and they are also good. On the other hand, there are set of atoms like this even carbon and nitrogen, all these oxygen flow including silicone phosphorous, all they are actually good for, ammonium will be large amount of secondary yields is possible when you CS+ primary ions.

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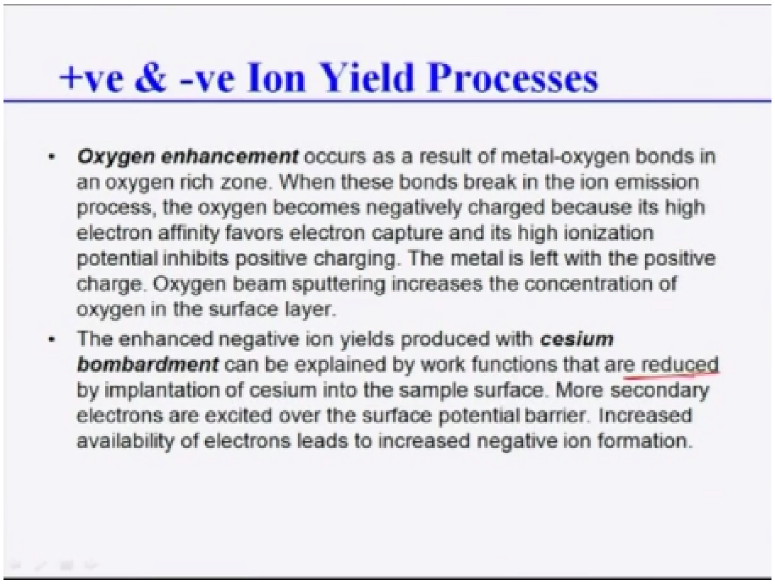

+ve & -ve Ion Yield Processes

- ***Oxygen enhancement*** occurs as a result of metal-oxygen bonds in an oxygen rich zone. When these bonds break in the ion emission process, the oxygen becomes negatively charged because its high electron affinity favors electron capture and its high ionization potential inhibits positive charging. The metal is left with the positive charge. Oxygen beam sputtering increases the concentration of oxygen in the surface layer.
- The enhanced negative ion yields produced with ***cesium bombardment*** can be explained by work functions that are reduced by implantation of cesium into the sample surface. More secondary electrons are excited over the surface potential barrier. Increased availability of electrons leads to increased negative ion formation.

Well, so that means if I consider positive and negative ion and yield processes, then I need to tell you that oxygen enhancement occurs the result of metal oxygen bonds in their oxygen rich zone. So therefore those are the metals which will form very good metal oxygen bonds, then only they will form better secondary ion yields. When this bonds break in an ion emission process, oxygen becomes negatively charged, because of this high electron affinity which favors electron capture and its high ionization potential inhibits the positive charging.

So metal is left with the positive charge, so oxygen beam sputtering increases the concentration of oxygen in the surface layer. Because oxygen actually thus molds with metal and forms this bond and then its bear bond breaks, oxygen ion remains then metal ion gets comes out. Enhanced negative ion yield that normally produced by cesium bombardment, and this is can be explained by work function that are reduced by implantation of cesium into the sample surface.

More secondary electrons are excited of the sample potential barrier, and this is to increase availability of electrons leading to increase negative ion formation. So, as you clearly understood now that oxygen bombardment will lead to positive ion creation, cesium bombardment leads to negative ion creation. So therefore, a metal in which positive ion creations are easier, all metal positive ions gets easier, but oxygen absorption easier is that is oxygen enhancement.

And other things metalloids are even, some other metals basically metal like copper or things here, it is so new, zinc, sorry copper, silver, gold and the heavy metals like bismuth, metalloid, bismuth and too many tin, allodium you can use cesium.

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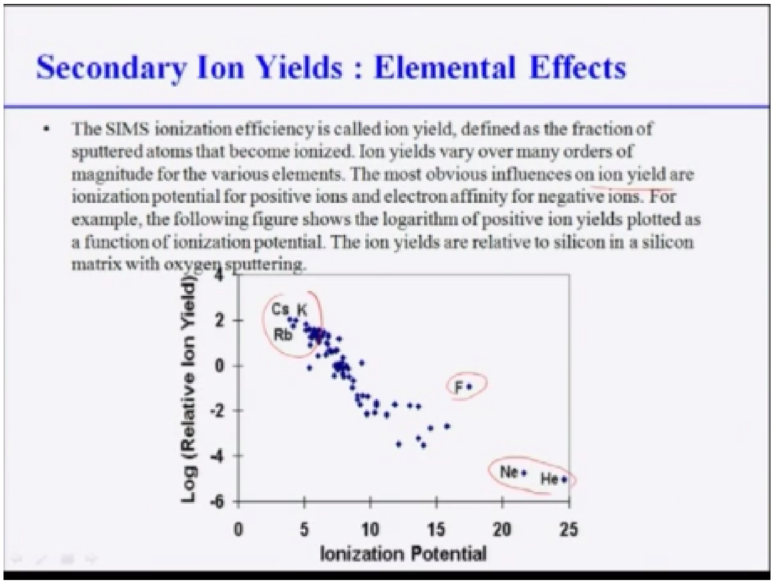

Secondary Ion Yields : Elemental Effects

- The SIMS ionization efficiency is called ion yield, defined as the fraction of sputtered atoms that become ionized. Ion yields vary over many orders of magnitude for the various elements. The most obvious influences on ion yield are ionization potential for positive ions and electron affinity for negative ions. For example, the following figure shows the logarithm of positive ion yields plotted as a function of ionization potential. The ion yields are relative to silicon in a silicon matrix with oxygen sputtering.

Obviously, secondary ion yields depends on elements, type of elements which we are dealing with. Secondary ion efficiency is very well defined things; it is nothing but fraction of this sputter ion that becomes ionized. You have large number of sputter atoms, all it 10 or 50% atom becomes ionized. That fraction is known as secondary yield. As you know, ion yields vary over many orders of magnitude, but different various elements that means there is an elemental effect.

The most obvious influences on the ion yields are basically ionization potential for positive ions. Ionization done in potential is very hard to create; it is a sputtered atom, not an ion, and also electron affinity of the negatively charged ions. For example, this figure actually shows logarithmic positive ion yield as a function ionized potential. Ion yields are related to silicon and silicon matrix with oxygen sputtering.

So what you see here, cesium, ruthenium and the uranium and potassium has a very high ionization yield, whereas uranium, neon and helium has a very low ion yield. In fact, who is also in a borderline case? So ionization potential is high means less ion yield, ionized potential low more secondary ion yield, that is obvious because then only we can create more ions by removing the electron. So that is actually how the secondary ion yields depend on.

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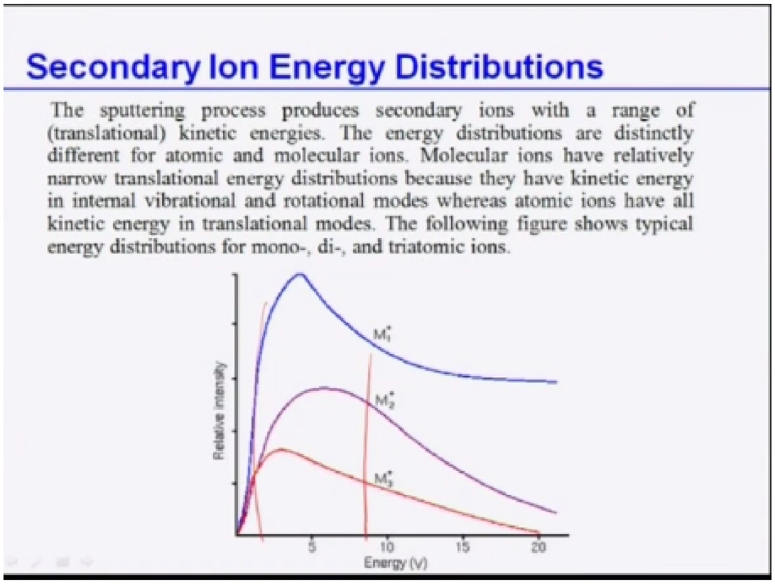

Secondary Ion Energy Distributions

The sputtering process produces secondary ions with a range of (translational) kinetic energies. The energy distributions are distinctly different for atomic and molecular ions. Molecular ions have relatively narrow translational energy distributions because they have kinetic energy in internal vibrational and rotational modes whereas atomic ions have all kinetic energy in translational modes. The following figure shows typical energy distributions for mono-, di-, and triatomic ions.

Not only that, secondary ion has kind of different energies, because we can secondary ions but whether they will be able to travelling to the detector or we will be able to collect them or not, depends on the energy distribution. Sputtering process produce secondary ions with range of kinetic energies, as distributions are distinct different for atomic and molecular ions. Molecular ions are always elective and narrow translational energy distribution, because the kinetic energies in the internal vibration and rotational modes.

Whereas, atoms atomic ions have kinetic energies in translational modes. So following this figure actually showing us mono-, di- and triatomic ions. As you see, relative intensities of the monoatomic ions are much larger than bi- and triatomic ions that is understandable because as the number of ions increases, actually charge increases, they will have less probability to presence.

So as you see this is the plot of the radius of energy, so only in a particular energy window between about 2 to 8 Coles, you have relatively high intensity of all the different types of ions.

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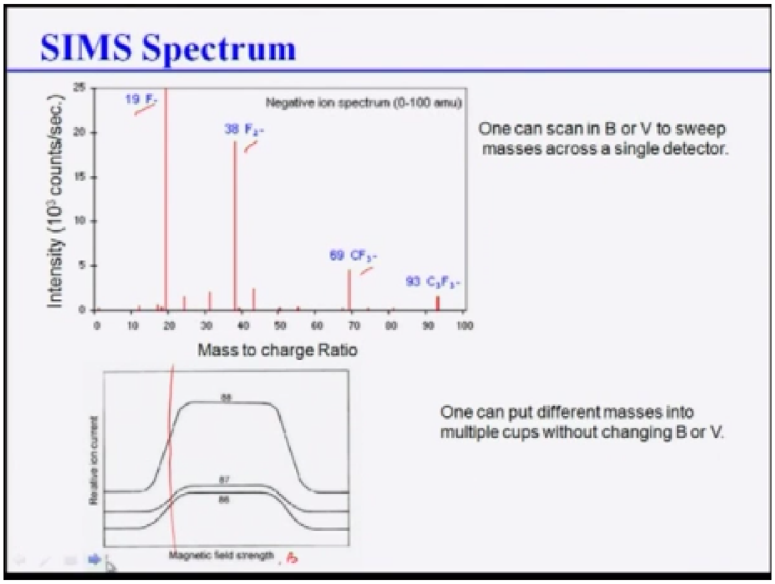

SIMS Spectrum

One can scan in B or V to sweep masses across a single detector.

One can put different masses into multiple cups without changing B or V.

So, I have given you a lot of idea about primary ions, sputtering, yield up secondary ions, and also the pack that control the secondary ion yield. Let me just give you some idea about how SIMS spectrum looks like. SIMS spectrum can be plotted in two ways; first one is on the top which is nothing but a plot between intensity versus master charge ratio. One can actually scan in B and V that is negative field or voltage starting electron speed applied or to fill mass in a single detector.

As you see, this is a fluid ion, these fluid 2 ions, this is CF3 ion, this is C2, and we can distinctly difference between this negatively charged ions depending on this master charge ratio. Not only that, we can even quantitatively calculate on these intensities; how much of 19 mass by charge, mass actually fluid ions are present or the double ions are present CF3 or C3F3 – ions are present or not.

This is one way of plotting the data; other way of plotting the data is to plot the different masses into multiple graphs without changing the B&V. In this case, you are changing B and V in the top picture, so it can swipe all the masses. Here we are not changing B and V we are basically having different masses as a graphs, this relative ion current passes 90 fields 10 that is B. As you see here, in a constant B value you have different relative ions for an 87, 86 atomic number species.

So you get a cup like picture whenever you plot for the whole magnetic fields, for the large range of magnetic fields.

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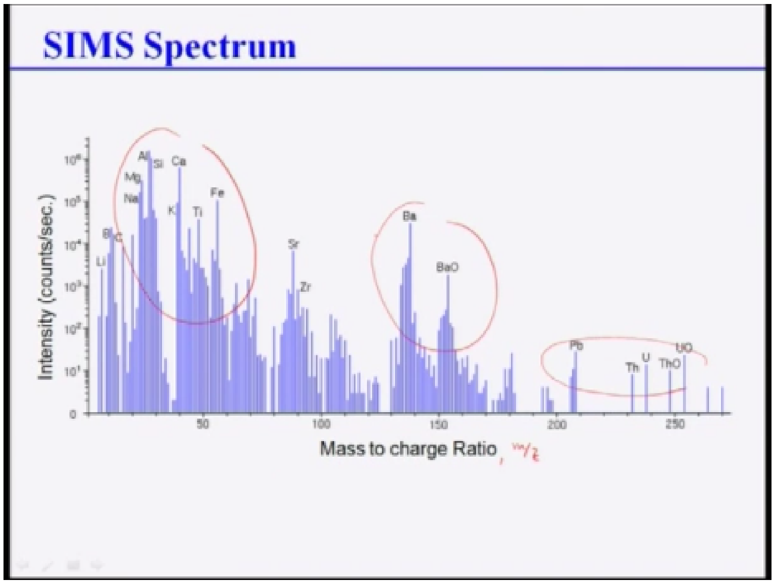

SIMS Spectrum

So you can basically get a cup, and this cup gives you different charge species. If you plot, basically SIMS can measure starting from lithium to uranium. So if you want to show the integrative intensities of the pix for different metals, this is the best one. Here I am showing the intensity versus mass to charge ratio. What you see here is basically starting from lithium to uranium m/z values and intensities.

So, as you see here certain, the m/z is in a low than actually certain area like this, you have very high intensity, all 10^6, 10^5 count per second. Whereas here if m/z is very high, lead, thorium, uranium even high numbers. So you can see the yield is, the intensity is low. You can actually see even that intensity is low for even barium, barium compounds also. So that means the intensity of these secondary ions which is detected by detector. It depends also on the mass by charge ratio.

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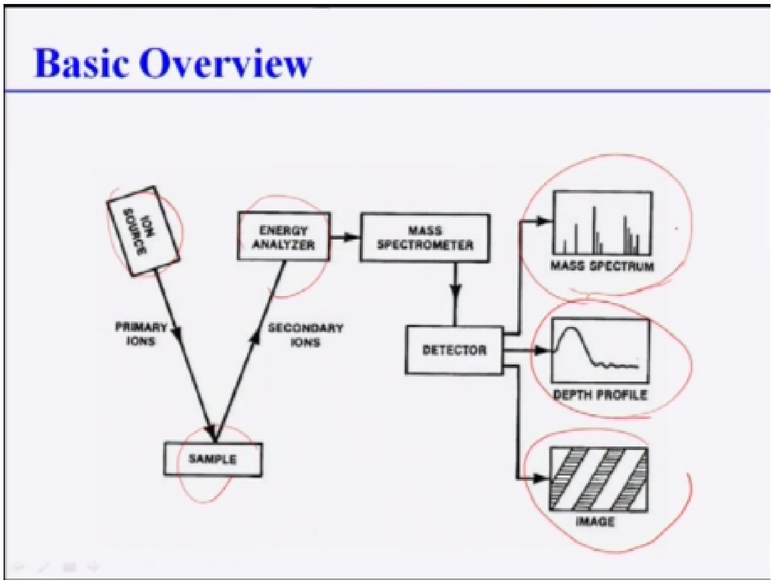

Basic Overview

So the secondary ion mass spectroscopy, what all things are there, really I have discussed about the ion source, primary ions, you need sample? Primary ions comes and heat the sample, create secondary ions, then you have an energy analyzer or other energy grabbers, the secondary ion grabber which grabs and analyze the energy, and this ions are then passed to the mass spectrometer.

And then we separate ions depending on m/z values and you detect. So you can actually have a mass spectrum which I have shown you, you can also have a depth profile which I am going to discuss, was important material science, and you can actually also create an image or two dimensional image, actually truly speaking, you can clear the three dimensional image also in the SIMS, this is so powerful technique.

So this is the one I have shown you that why I wanted to show you these before, I show the basic overview. Now I am going to show you how depth profile, quantification, and image formation is done.

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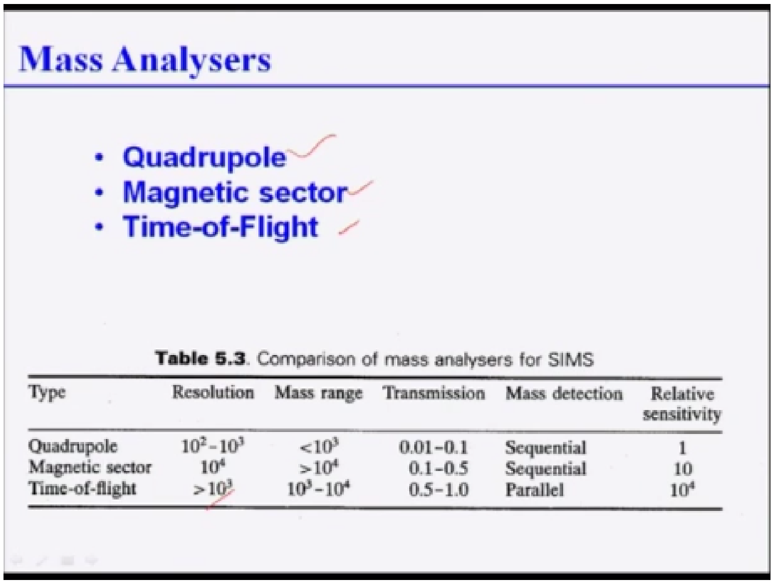

Mass Analysers

- Quadrupole
- Magnetic sector
- Time-of-Flight

Table 5.3. Comparison of mass analysers for SIMS

Type	Resolution	Mass range	Transmission	Mass detection	Relative sensitivity
Quadrupole	10^2-10^3	$<10^3$	0.01–0.1	Sequential	1
Magnetic sector	10^4	$>10^4$	0.1–0.5	Sequential	10
Time-of-flight	$>10^3$	10^3-10^4	0.5–1.0	Parallel	10^4

Well, as I said, these are different mass analyzer use and the idea is to show you how their relative behavior is. You have Quadrupole mass spectrometer with resolution of 10^2 10^3 that means 100 to 1000, mass range can be detected less than 1000, transmission is pretty low in all the case but it is lower in Quadrupole, mass detection is sequential 1 /1, sensitivity in a scale of 10,000 that is 1.

If you use magnetic sector that graph magnetic sector that I have shown you it is relates 10^4 10,000, mass ranges can be very high that means you can detected 10^4 and higher, transmission is also quite high, quite high means higher than the Quadrupole 0.1 to 0.5, again measurement sequential. Sensitivity is better than Quadrupole, but not very high, best one is, that is what I said to you in the lecture, is time of flight.

Time of flight has a high resolution 10^3 or higher, it can scan masses 10^3 to 10^4, it has very good transmission approximately close of 1, it can detect masses parallely sequence not sequence and parallely together, that is an advantage, and it has very high relative sensitivity 10^4, 10,000, so that means time of flight is very strong. So therefore, we can clearly see that time of flight is the best option for us or for the SIMS. And that is why it is so widely used in a different machine.

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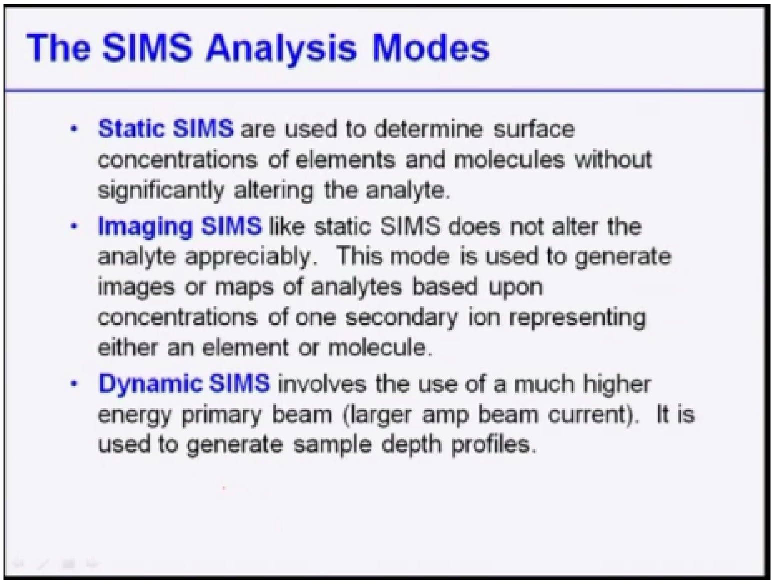

The SIMS Analysis Modes

- **Static SIMS** are used to determine surface concentrations of elements and molecules without significantly altering the analyte.
- **Imaging SIMS** like static SIMS does not alter the analyte appreciably. This mode is used to generate images or maps of analytes based upon concentrations of one secondary ion representing either an element or molecule.
- **Dynamic SIMS** involves the use of a much higher energy primary beam (larger amp beam current). It is used to generate sample depth profiles.

Now SIMS analysis can be done in different ways, the most widely used one is static SIMS which are used to determine surface concentration of elements, and molecules without significantly altering the sample. Then you can image SIMS that is what I said like few minutes back like static SIMS does not alter the sample appreciably, this mode used to generate the images or maps based on the concentration of the secondary ion representing either element or molecule.

You can have also a dynamic SIMS involved in the use of a much high energy beams primary beams, but it is used to generate normally depth profiles, not the two dimensional profiles. So along with depth you can measure the concentration.

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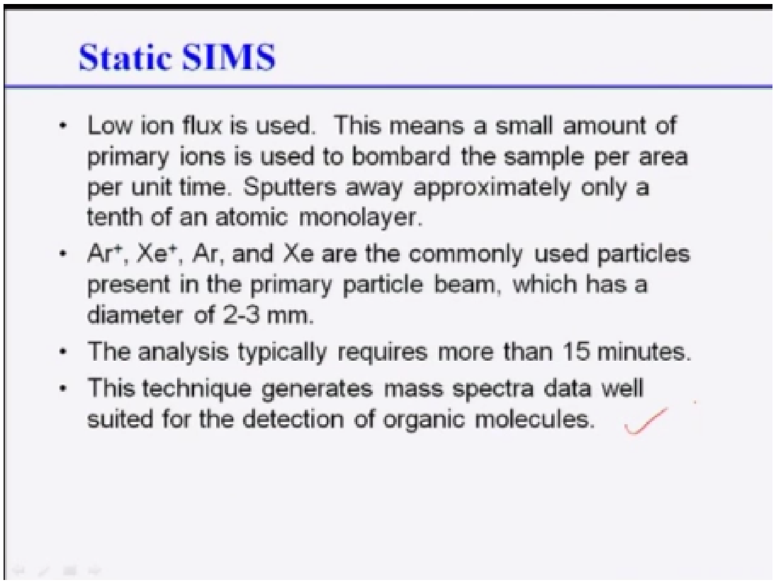

Static SIMS

- Low ion flux is used. This means a small amount of primary ions is used to bombard the sample per area per unit time. Sputters away approximately only a tenth of an atomic monolayer.
- Ar^+, Xe^+, Ar, and Xe are the commonly used particles present in the primary particle beam, which has a diameter of 2-3 mm.
- The analysis typically requires more than 15 minutes.
- This technique generates mass spectra data well suited for the detection of organic molecules.

In the static SIMS actually you can use low ion flux, this means a small amount of primary ions are used bombard the sample per unit time. Sputters away approximately only 10^{th} of an atomic monolayer, very small flux, so we use thermally argon, xenon, ions and it has diameter of very small as 2-3 mm. The analysis typically requires more than 15 minutes to generate some mass spectra data well suited for detection of the organic molecules.

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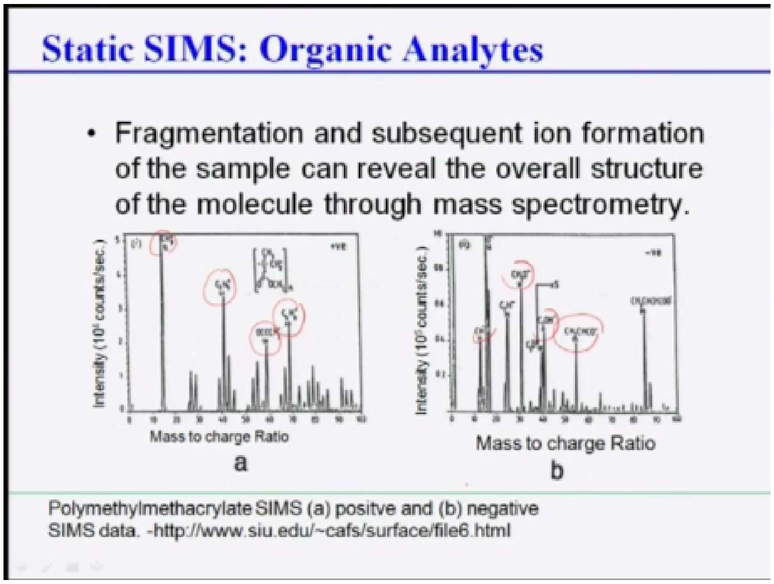

Static SIMS: Organic Analytes

- Fragmentation and subsequent ion formation of the sample can reveal the overall structure of the molecule through mass spectrometry.

Polymethylmethacrylate SIMS (a) positve and (b) negative SIMS data. -http://www.siu.edu/~cafs/surface/file6.html

To give you some results, it is taken from polymethylmethacrylate SIMS both positive and negative SIMS data, see that you can actually define, I do not know whether you can see C3H5+C3H5 C2H5 or this kind of DCO6 C3H5 things positive ions, and negative ions if you use like cesium are things which can create that you can actually, these different negative ions CH3O-, C3OH-, C2CHO- or these ones.

So depending on the different positive and negative ions, you can actually detect all of them using this static SIMS, fragmented subsequent ion formation of the sample can reveal well structured molecule to the mass spectroscopy is possible to do.

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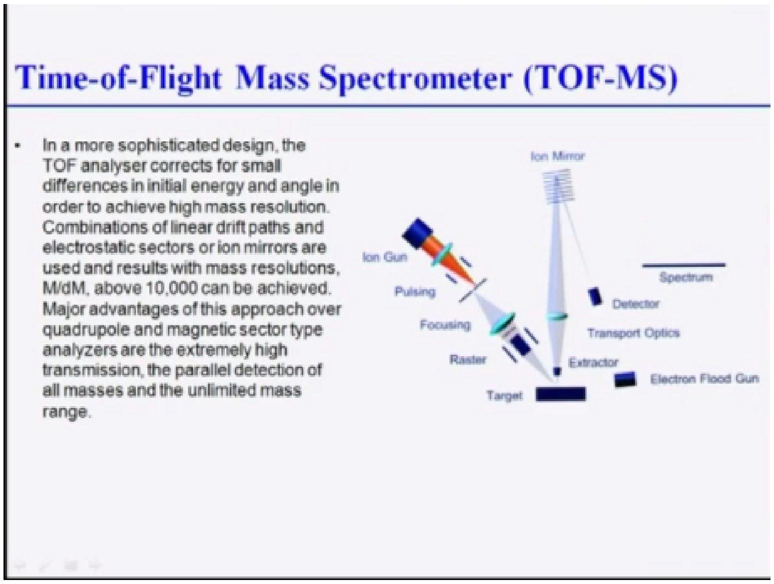

Time-of-Flight Mass Spectrometer (TOF-MS)

- In a more sophisticated design, the TOF analyser corrects for small differences in initial energy and angle in order to achieve high mass resolution. Combinations of linear drift paths and electrostatic sectors or ion mirrors are used and results with mass resolutions, M/dM, above 10,000 can be achieved. Major advantages of this approach over quadrupole and magnetic sector type analyzers are the extremely high transmission, the parallel detection of all masses and the unlimited mass range.

Next one is which I have already discussed is the time of flight. Time of flight is the most notable one, here actually you have ion gun which can pulsed and actually rested also. And primary ion falls on a sample surface, then secondary ions are generated. You can extract the secondary ions by using extractor and then it passes to a long distance and they actually extract and accelerate the same kinetic energies, depends on the both kinetic energy reach on same at the beginning.

And when they travel a long distance, the time of flight varies by this where you can detect. This is a sophisticated instrument as I said and used for many application.

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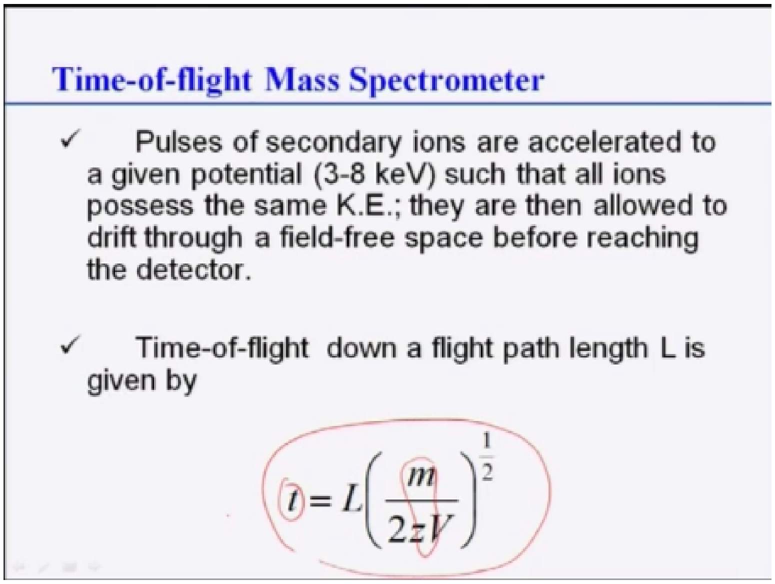

Time-of-flight Mass Spectrometer

- ✓ Pulses of secondary ions are accelerated to a given potential (3-8 keV) such that all ions possess the same K.E.; they are then allowed to drift through a field-free space before reaching the detector.
- ✓ Time-of-flight down a flight path length L is given by

$$t = L\left(\frac{m}{2zV}\right)^{\frac{1}{2}}$$

And so this is the equation I have showed you, so depending on the m/z values you can have different time scale, and they can detect it.

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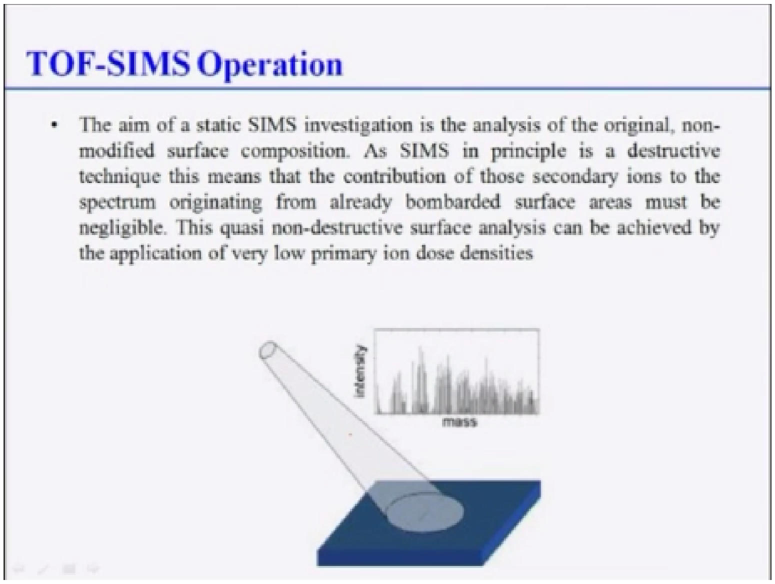

TOF-SIMS Operation

- The aim of a static SIMS investigation is the analysis of the original, non-modified surface composition. As SIMS in principle is a destructive technique this means that the contribution of those secondary ions to the spectrum originating from already bombarded surface areas must be negligible. This quasi non-destructive surface analysis can be achieved by the application of very low primary ion dose densities

SIMS and time of flight operations actually very popular one, it uses a destructive technique, you can remove the sample and measures the secondary ions. And then one by one layer removal was possible and measure the compressions one by one, so that it is used, you have a sputtered ions and then time of flight, and then online mass spectrometer.

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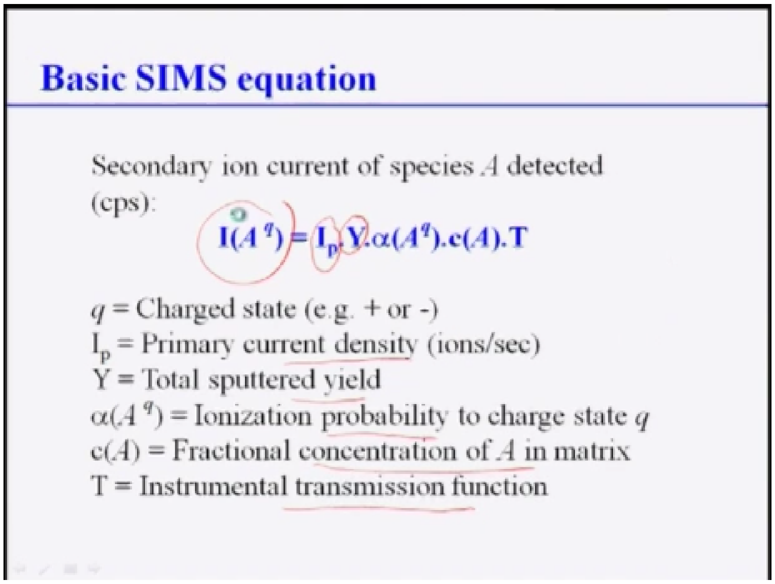

Basic SIMS equation

Secondary ion current of species A detected (cps):

$$I(A^q) = I_p.Y.\alpha(A^q).c(A).T$$

q = Charged state (e.g. + or -)
I_p = Primary current density (ions/sec)
Y = Total sputtered yield
$\alpha(A^q)$ = Ionization probability to charge state q
$c(A)$ = Fractional concentration of A in matrix
T = Instrumental transmission function

Well, you should also know some amount of aspect above the intensity or species of the secondary ions and this is basically equal to $Ip.Y.\alpha(q).c(A).T$. As you see this basically depends on primary current density, total sputtered yield of the primary current. A is nothing but ionization probability of the charge state q, c(A) is the fractional concentration of the element A in a matrix, and T is instrumental transmission function.

So, transmission function is that is why I have shown you in the slide before, so as you see, this is strong personal I_p and Y that is why we discussed about the primary current, primary ions and this sputtering yield. They are actually determined with α and other factors exactly secondary ion concentration species.

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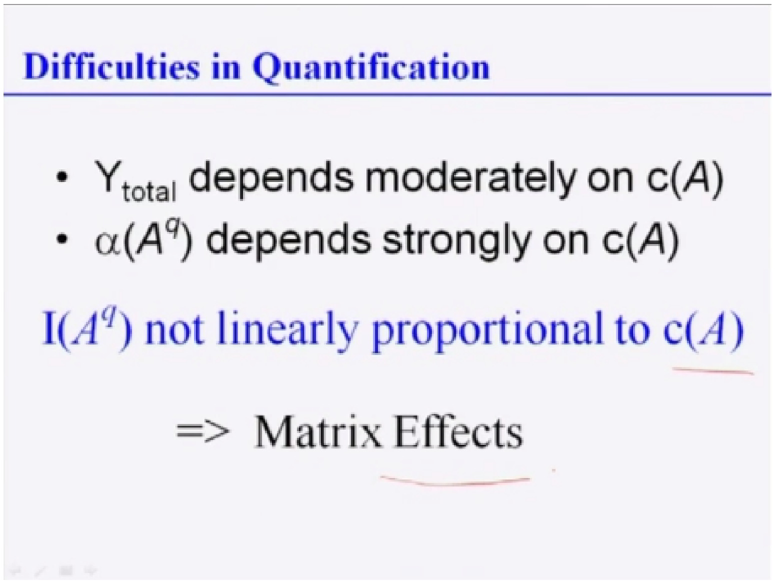

Difficulties in Quantification

- Y_{total} depends moderately on $c(A)$
- $\alpha(A^q)$ depends strongly on $c(A)$

$I(A^q)$ not linearly proportional to $c(A)$

=> Matrix Effects

Well, there are problems in using these data, but this is what is the total intensity and this can be used to quantify and there are problems, the problems is that Y_{total} depends moderately on c(A) and α also depends strongly c(A). So this is basically that means I of industrial secondary ion is not lineally proportional c(A) and there will be matrix effects. That is why sometimes, it is not possible to measure exactly to quantify these things there is always some error involved.

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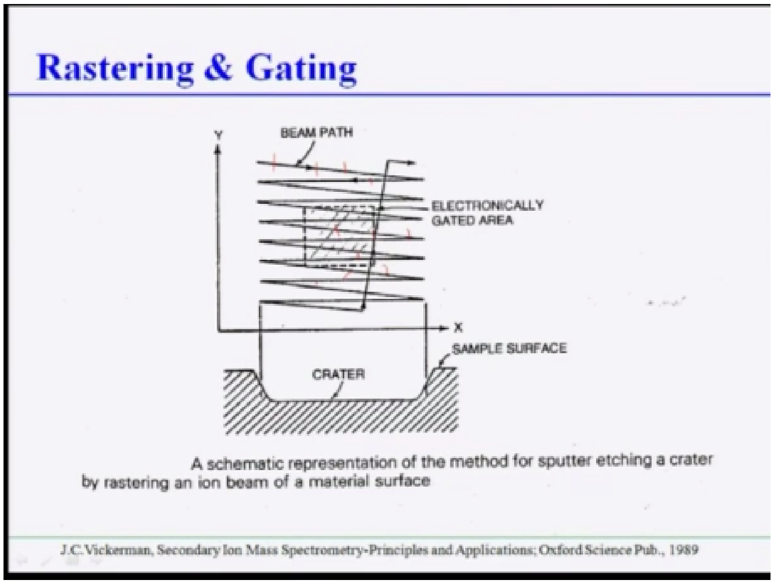

Rastering & Gating

A schematic representation of the method for sputter etching a crater by rastering an ion beam of a material surface

J.C.Vickerman, Secondary Ion Mass Spectrometry-Principles and Applications; Oxford Science Pub., 1989

Well, SIMS can also be used to raster or getting time applied it is done, and if you have a defined path, this is the beam path, you can see here the beam path follows like this, so this is nothing but electronically gated area, you can actually create a crater and as you raster, every point you can measure the SIMS profile by time of flight. And once you do that every point you measure you can actually get the compulsion values and by this you can create a three dimensional map.

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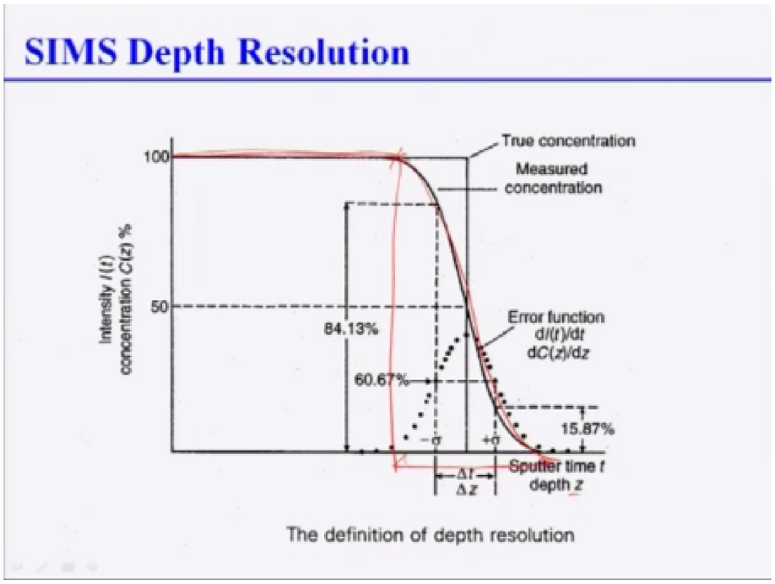

SIMS Depth Resolution

The definition of depth resolution

Another important thing which SIMS allows you to do is depth profile. What is it, well, one can actually do, slowly remove the material sample surface in the depth direction to measure the concentrations. Well, the important aspect in such a case is a depth resolution. What is showing here is intensity and concentration of the certain species as a function in a sputtering type or the depth?

As you see here, this is the 100 time intensity which is good till certain time and then it falls off near the surface. So that means this is good in this region, not good in that region okay. So that is what actually can be done in a SIMS depth resolution profile.

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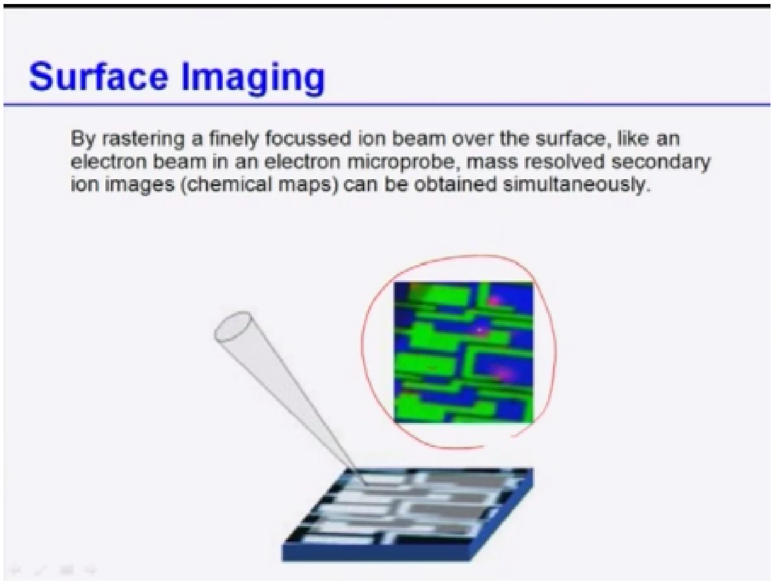

Surface Imaging

By rastering a finely focussed ion beam over the surface, like an electron beam in an electron microprobe, mass resolved secondary ion images (chemical maps) can be obtained simultaneously.

One can actually use SIMS for kind of imaging or surface imaging because you can raster. So if you can raster, you can actually image by rastering a finely focused ion beam over a surface like this and one can actually create mass resolved secondary ion images. This is basically nothing but scanning electro-microscopic image, but here we are mass resolved secondary.

And as you see here if I have a primary beam, which I can raster on a sample and then each point we can channel it secondary ions and after measuring secondary ion types and yield of that and quantifying the different elements, we can actually create a map. Just like elemental map in this case, you different pix from different elements comes, and then from a particular point, and measuring the peak intensity you can measure and quantify the particular element.

And with an map, it is exactly done here same thing, you can use instead of the electron microscope using this in a secondary ion mass spectroscopy. And this what a picture you get, colorful picture you see here, it shows you concentration of the three different species, one is green, blue, and little bit red, so that means it is possible.

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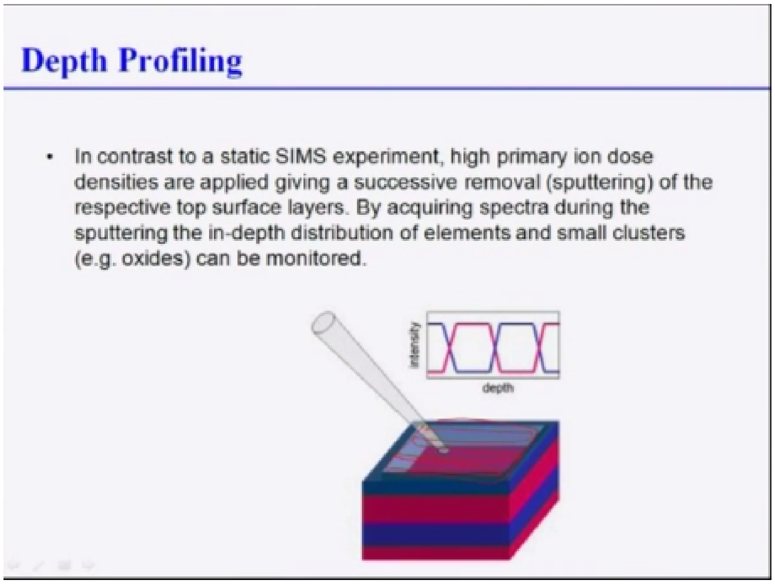

Depth Profiling

- In contrast to a static SIMS experiment, high primary ion dose densities are applied giving a successive removal (sputtering) of the respective top surface layers. By acquiring spectra during the sputtering the in-depth distribution of elements and small clusters (e.g. oxides) can be monitored.

Not only that, it is possible to do depth profiling and in contrast to a static SIMS experiment, but dynamic ones actually high primary those densities can be applied in this, and it can give successively well on the respective top surface layers, and by occurring spectrum at the end of the sputtering, the in-depth distribution of elements and small clusters can be monitored. So as you see here, this is a volume which is sputtered slowly and raster also obviously.

So you just start from this part and then go and then it come back with raster. So one surface layer is removed and you move the composition. Then you go in the depth direction, and then do the same thing rastering and get the distribution of elements in a three dimensional, or otherwise you can actually keep the beam constant static, do not do the beam and just sputter on a certain directions and measure constants from the elements.

Obviously, I have given you a lot of examples, different examples, all sorts of examples I have given. As you see here, one must know very clearly that there are very advanced measurements can be done using SIMS.

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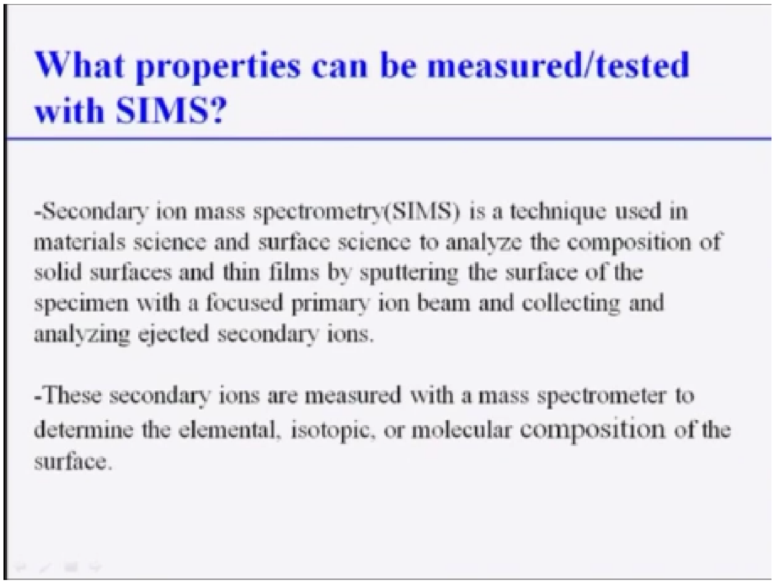

What properties can be measured/tested with SIMS?

-Secondary ion mass spectrometry(SIMS) is a technique used in materials science and surface science to analyze the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions.

-These secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface.

It is a technique which is used extensively in material science and surface ions to analyze the composition of solid surfaces and also thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing the ejected secondary ions. Secondary ions are then measured using mass spectrometer, you can do elemental, isotropic, molecular composition to surfaces.

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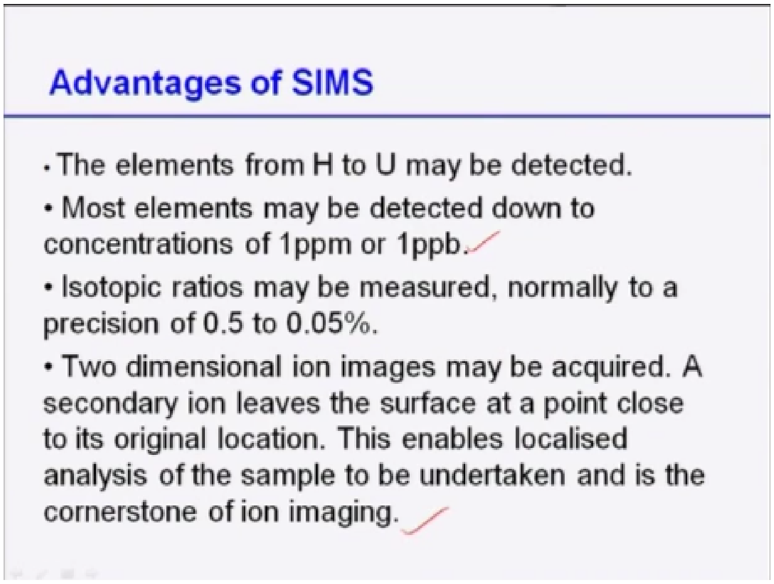

Advantages of SIMS

- The elements from H to U may be detected.
- Most elements may be detected down to concentrations of 1ppm or 1ppb.
- Isotopic ratios may be measured, normally to a precision of 0.5 to 0.05%.
- Two dimensional ion images may be acquired. A secondary ion leaves the surface at a point close to its original location. This enables localised analysis of the sample to be undertaken and is the cornerstone of ion imaging.

Actually you can do, I could measure elements from higher than uranium not higher that actually you can do lithium to uranium very easily, you can actually detect element down to concentration from 1ppm to 1ppb. Isotopic ratios can be measured; isotopic means oxygen theory of isotopes. What are the amendments of the isotopes it can be done normally to reason of 0.5 to 0.05% which cannot be done by using any other techniques.

You can actually do two dimensional ionic image measurements, the ionic images which I shown you, the secondary ion leads to surface a point close to the original location, this enables, localized analyze some sample to be undertaken any correction as a cornerstone of the images. So not only that you can actually have three dimensional ion images can be acquired by scanning or rastering the primary beam and relating that.

It requires very little sound pressure relative to and surface I like and I see on the TM you do not require much sample versions, and it can actually do many other things, you can actually material sputter actually you might be thinking material sputter is a large, no. Sputtering is few fractions of distance of the atomic layer on the surface, so sputtering is small without damage, but only when you dynamic SIMS you damage the sample surface but there are problems. And so I have just given you three dimensional image following the image sputter is small I told.

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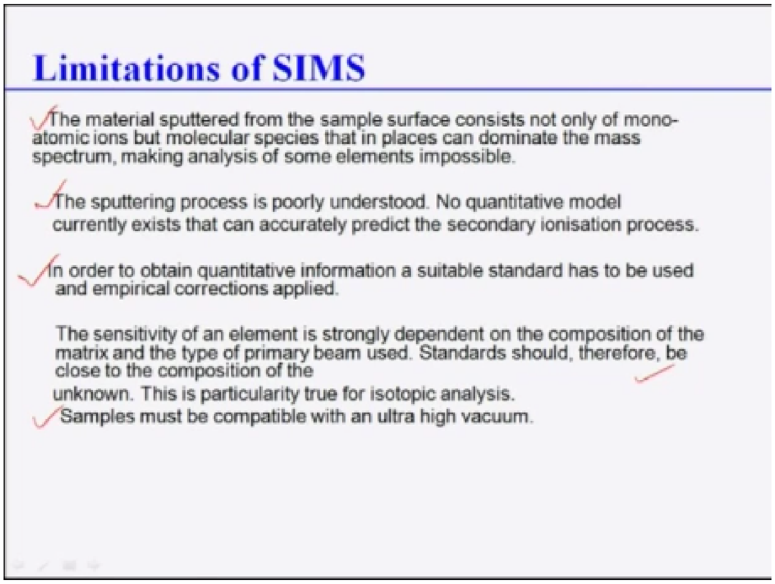

Limitations of SIMS

The material sputtered from the sample surface consists not only of mono-atomic ions but molecular species that in places can dominate the mass spectrum, making analysis of some elements impossible.

The sputtering process is poorly understood. No quantitative model currently exists that can accurately predict the secondary ionisation process.

In order to obtain quantitative information a suitable standard has to be used and empirical corrections applied.

The sensitivity of an element is strongly dependent on the composition of the matrix and the type of primary beam used. Standards should, therefore, be close to the composition of the
unknown. This is particularity true for isotopic analysis.

Samples must be compatible with an ultra high vacuum.

But it has some limitations; it is not a full put technique. The method limitation of this technique is that the material is part of a sample surface not only consist of monoatomic ions, but also consists of molecular species. That in species can actually dominate the mass spectrum and making an analysis of this element is impossible. It is very obvious, because you have high energy primary source, and this high energy primary source can bombard and create molecular species like CH4+, CH3+, CH3- these species can be created in organic things, many others.

Normally metals are possible, but you can create metal complexes, because cascade of this primary ion event can lead to mixing, and mixing the lead to even formation of the metal complexes. Second important thing which is bad about this whole sputtering process which is the main thing in SIMS, it is very poorly understood. We do not have any quantitative model so far that can accurately predict the secondary ionization process that is known.

So that is actually makes us assume certain things for the secondary ion generation process. And because, and that assumption actually makes the technique little bit less attractive in a sense that we do not know really how the secondary ions actually created or the process, so we have no idea. We can measure the yields and other things but we have no idea or theoretically, also we cannot modulate.

Third thing is that to obtain a quantity information of the suitable standard you have to have a quantitative for suitable standard and that is the case for everything, you know, in a same also EDS also requires measurements of these requires a standard. Third thing is the sensitivity of the element is strongly depends on the composition of the matrix so we are putting element in a organic matrix, liquid matrix.

So it depends on the matrix soon there, even the intensity is also the function of the matrix, it is not linear with only that element present. And also type of primary beam that we do used, 6 standard should there for the close of the composition of the unknown. This is particularly true for the isotopic analysis. Lastly, sample which you are doing must be compatible with high vacuum; it is degrading inside the vacuum, because we are using a very high vacuum system.

Because we are using a very high vacuum system + or – fixed, 7-9 to -10 torque under the vacuum, it should not transform or it should not degrade to anything else that is basically a good limitation for that. Otherwise, it has many advantages, and so with this I actually close this discussion on this SIMS. And only thing I need to do is to compare these three techniques extended like SPS, RGO and the SIMS and tell you how these techniques can be used in different things.

Acknowledgement
Ministry of Human Resources & Development

Prof. Phalguni Gupta
Co-ordinator, NPTEL IIT Kanpur

Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

Camera
Ram Chandra
Dilip Tripathi
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Shikha Gupta
Pradeep Kumar
K.K Mishra

Jai Singh
Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

Light & Sound
Sharwan
Hari Ram

Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

Production Manager
Bharat Lal

an IIT Kanpur Production