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Module No. # 10 Lecture No # 28 Chemical and Compositional Characterization: XRD and AFM

Welcome, to the 28th lecture in our particle characterization course. In the last lecture, we started discussing methods of chemical and compositional analysis of particles and we noted that there were several methods available that could enable us to characterize inorganic materials as well as organic materials; all of them really start with microscopic inspection.

First, you have to be able to see the particle before you can analyze it, so we use some means of magnification whether it is optical or whether it is by electron impingement - in order to obtain a magnified image of the particle; subsequently, we can proceed to strike the particle with various energy sources in order to get appropriate descriptions of the chemical makeup of the particle.

For example, x-rays give us actual species information - the molecular structure of the compound; whereas, simple electron scattering can enable us to - when you combine it with energy dispersive spectroscopic analysis - you can characterize the elemental composition of the particle and that is for inorganic particles; whereas, for organic particles we saw that essentially they work by the principle of absorption of either infrared light or monochromatic visible light and the absorption spectrum gives us an idea regarding the actual composition of the organic particle

So, methods such as FTIR spectroscopy and Raman microprobe are widely used for doing organic particle analysis. There are other methods such as ion chromatography which can also be used to identify the composition of particles particularly when they are dissolved in liquids.

An ion chromatograph essentially identifies and characterizes all ions that are present in a liquid solution.

However, if the particle is present in an insoluble form then an ion chromatograph will not be able to identify it, because it depends on taking the solution and running it through a chromatographic column in order to characterize the ions that are present.

Similarly, there is a technique called gas chromatography which again requires that the organic particle that is on the surface or organic film must be soluble in some solvent, then you can solublise the organic material into the solvent and again you vaporize the solvent along with the particle that is dissolved in it and you take the vapour through a gas chromatographic column; by looking at the kinetics of passage of this vapour through the column you can identify the chemical composition of the particle; you can combine this gas chromatograph with mass spectra meter in order to do identification of the species by tracking the mass of the different species.

Essentially, the idea is that organic species of high molecular weight will travel slowly through the column; so, by looking at the spectrum as a function of time of passage through the column you can actually classify the various organic materials that are present in your solvent and thereby identify the particle that was there begin with; but, again, this requires that the organic material, whether it is a particle or a film, must be soluble in some solvent which can be used for this g c m s type of analysis.

Now, there are materials that are called non-volatile residues - these are particles that are on a surface which cannot be vaporized under normal conditions; we will have to go to extremely high temperatures and extremely low pressures in order to be able to vaporize these particles and that is the reason they are called non-volatile.

Many of these are also not very soluble in most solvents, so the analysis of such low volatility particles on surfaces and in liquids really requires that we have to go back to our microscopic techniques.

You essentially have to filter such particles on to a holder and then subject that sample holder to a microscopic inspection to obtain the physical nature as well as the chemical composition of the particle.

So, what you need to do is to customize your identification technique to the particle at hand; the same technique cannot be used for all particles of all types; size is also a critical parameter - it is obviously much easier to analyze larger particles. Typically, low

magnification will suffice and even chemical analysis techniques - I mentioned yesterday, that FTIR spectroscopy is useful for particles in the 10 micron and larger size range, which for a particle scientist is very large particle.

But, if you have particles that are especially in the nano range then many of the techniques that we have been discussing yesterday are really stretched to their limit; because, in order to do SEM, EDX on a nano particle is very difficult, because it requires extremely high magnifications; so, you need a lot of energy impinging on the particle and as you do that the resolution you measurement decreases.

So, you cannot accurately characterize its composition. In other words, you can either do physical characterization or chemical characterization accurately, but many times it is difficult to do both simultaneously; it kind of tends to sacrifice one for the other.

Especially, with organic particles, if you have an organic nano particle you have to keep increasing the incident energy to very high levels to be able to be see it and then it actually starts to change the particle; in extreme cases organic particle can actually start burning; or, you will have to coat it with some material to keep it from burning, but if you do that then it is very difficult to obtain the composition; because, that has be occluded by whatever coating you have imparted to the particle.

That is why it makes it a little tricky as particle size is decreased. The physical characterization may still be possible, where if you are simultaneously also trying to do chemical characterization that can introduce another level of complexity in your analysis.

So, two techniques have emerged in the past few decades that have been a real boon to nano technology and they are atomic force microscopy, and X R D - x-ray di-fraction analysis.

The advantage of these methods is that they do not - particularly, the atomic force microscope - it does not require any type of highly controlled and highly aggressive analysis environments; for example, an SEM or a TEM requires high vacuum, it also requires extensive sample preparation; an A F M can basically be done virtually in an open room environment like this; the main thing you have to be careful about is vibration, not so much the other factors that you normally would be concerned with.

What is Atomic Force Microscopy? Back in the early 80s IBM researchers in the Zurich lab came up with a technique called scanning probe microscopy for which they actually won a noble prize.

The atomic force microscope is essentially a variant of the scanning probe microscope; the only difference really is that a scanning probe microscope is particularly suited to conductive or semi conductive surfaces, whereas an atomic force microscope can be used for virtually any surface; the name itself is actually a misnomer an atomic force microscope is not a microscope at all because you are not looking.

Microscope, by definition, is something that you look through; an atomic force microscope is something that you feel through; because, you are actually contacting the surface with the physical object and by looking at the interaction between the probe that you are using to contact the surface and the surface itself, which may be a planar surface like this or it may be a particle, you can extract a lot of information about not only the physical nature of the particle but even the chemical nature of the particle; it basically works on a cantilever principle.

The idea is that if you take a probe very close to a surface it will start feeling the intermolecular forces that we have discussed in one of the earlier lectures; there is a repulsive force that comes into play as the two surfaces get closer to each other, as they move further away there is an attractive force - we call this the Lennard Jones potential or six twelve potential, if you recall; you may also recall the characteristic force curve.

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If you look at the distance of separation between the two surfaces and you look at the force of interaction between them, essentially we saw a curve like this where this is the 0 point and this is your equilibrium position; as one surface gets closer to the other surface than the equilibrium position they feel a mutually repulsive interaction - repulsive forces are dominant in this regime.

This is the repulsive regime and as the particles start moving away from each other attractive forces tend to dominate, so this region from here to here is an attractive interaction region; if you move far away from the particle there is essentially a zero interaction as two surfaces keep moving away from each other eventually they would not even know that the other exist.

These are the three regimes of inter particle or inter surface forces. The scanning probe microscope or the atomic force microscope actually takes advantage of this behavior in order to characterize surfaces.

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The way this is done is, if you have a surface of some kind you essentially bring a tip very close to the surface; this distance of separation is really of the order of 1 nanometer or so.

You get the probe very close to the surface; in fact, as we will see the probe can actually be made to contact the surface, so the distance of separation can be of the order of angstroms.

Now, what happens is, as you bring this probe tip close to the surface it feels this force if it gets sufficiently close it feels a repulsive force, if it is sufficiently far away it feels an attractive force.

If you could characterize that force that will tell you something about certainly the morphology of the surface; because, for example if I hold the tip at the same distance and scan the surface, let us say, in this direction then depending on the roughness the distance of separation between the probe and the surface will change; you can very easily map the surface roughness and it is very easy to do it in 3 dimensions - the 2 axial and transverse dimensions of the surface and in the vertical dimension.

The simplest use of an atomic force microscope, in concept, is characterizing variations in the profile of the surface; in essence, it is like a profilometer - the people use frequently - mechanical profilometers are very widely used as are laser profilometers to characterize surface roughness.

The atomic force microscope can certainly do that for you. But, how do you measure this force? Now, what is the problem with measuring that force? It is very weak in terms of if you really talk about the magnitude of the force this is going to be in pico newton's how do you measure that?

That was really the challenge that was overcome in the invention back in the 80s; the atomic force microscope in '86 - which was invented in '86 - really solved it in a unique fashion by saying that we will make use of the cantilever principle.

So, if this tip can be made to ride on what is known as a diving board shaped - actually it is looks more like this - cantilever, and suppose we shine a laser light here; now, what is going to happen is that laser light will be reflected and captured and you can have a photo multiplier which can take this signal and multiply ir many times and give you a reading.

So, what is going to happen is as this tip experiences a force even the slightest deflection will be amplified many times because of the cantilever arrangement and the change in the angle of the incident laser will also be changed by several orders of magnitude beyond what was measured as this force.

By making use of a laser light bouncing of the end of the cantilever, you can get a much stronger signal; even very small changes in the force of attraction between the tip and the surface can be magnified sufficiently to be captured very sensitively using this cantilever arrangement - that is basically how this works.

The advantages of this technique - or in principle you can even look at samples in liquids, it does not have to be done on a dry surface. That is a huge plus, because many of the other techniques we have talked about - the microscopic techniques - require a dry surface, whereas the A F M is equally capable of handling dry samples as well as wet samples.

The tip is obviously a very important constituent and it has to be precision-machined to nanometer dimensions; actually, if you look at the tip closely it does not have a sharp edge, it actually has a slightly rounded edge.

It kind of looks like this; this rounding radius, again, is of the order of nanometers or less - the smaller the rounding radius the more sensitive and higher the resolution that you can get from the atomic force microscope.

The principle behind this is the Hooke's law, which I assume you have heard of. Hooke's law basically says that the force can be related to a stiffness constant k and deflection.

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So, by knowing the deflection through this cantilever arrangement and by knowing this stiffness constant for the particular probe-cantilever arm arrangement that you have selected, you can calculate what F would have been and from that you can characterize many things about the surface; because, what is this F a function of? F is basically the intermolecular or inter particle force.

This is a combination of the Van der Walls forces plus electrostatic forces plus capillary forces plus bridging forces plus chemical forces and so on; I mean, it is a net force. If you recall our lecture on particle adhesion to surfaces, there are many contributors to particle to surface adhesion and this technique - atomic force microscope - does not distinguish between the various contributions to the total adhesion force, but characterizes the net or sum of all the adhesion forces.

As the distance between the particle and the surface changes each of these forces will change as well; therefore, the atomic force microscope is a very sensitive detector of changes in surface morphology - it can even detect grain boundaries that are nanodimensional; there are very other techniques that are really able to do grain detection under essentially environment conditions, rather than in high pressure I mean low pressure type of environments.

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How do you use this technique for chemical characterization? The way you can use this is - supposing you have a surface that has a certain profile, and let us say that there is also a compositional variation on the surface.

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Now, as you know all these forces are also dependent on the nature of the material; for example, the Van der Walls force, if you recall, is related to the Hamaker constant and the Hamaker constant is very much of function of the material.

These forces are not going to change only because of physical variations in your sample, but also because of chemical variations.

You can actually distinguish 2 chemical elements that are adjacent each other simply by looking at the force that they impart to this atomic force microscope probe.

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So, chemical characterization also becomes possible; now, atomic force microscopy one of the requirements though is that it can sample surfaces very easily; but, supposing you are trying to characterize a particle that is sitting on a surface - can we do that using an atomic force microscope? The key thing is that the particle must not move during the sampling.

It must be held in place, which means it can certainly be used for particles that are strongly adhered to the surface, but for particles that are very loose on the surface, the use of an atomic force microscope involves some risks, because as you bring the probe close to the particle it can actually knock the particle of the surface by exerting sufficient force on it.

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So, if you want to analyze surfaces or if you want to analyze strongly bonded particles to surfaces there is no problem with using an A F M, but if you want to characterize loosely held particles on the surface then you have you can still use the A F M but you have to use it very carefully. Here, we have to be aware of three modes of operation that you can identify for an atomic force microscope, depending on how close the probe is to the surface.

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Atomic force microscopy can be done by bringing the probe into the repulsive region by bringing the probe very close to the surface; that is called contact A F M; or, you can do the analysis by taking the probe very far from the surface and that is called noncontact A F M; or, you can operate in an intermediate regime where you have intermittent contact or it is also known as tapping A F M.

So, the contact A F M technique works in this range; non-contact in this range, and intermittent bridges the two (Refer Slide Time: 21:49)

What is the difference? And when do you use what? Contact A F M is where you actually bring the probe close enough to the surface that the interaction between them is repulsive. The force of interaction is highest in the repulsive mode, as you can see, as the particles or surfaces come closer together the intermolecular force increases very rapidly.

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So, F values are very high in the contact mode; when you look at F contact, typically it is much greater than F non-contact and it is somewhat greater than F tapping.

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What that means is that for the same stiffness as you increase the contact force there will be more deflection; that is why it is called contact A F M, because when you bring the probe this close to the surface it is very difficult to prevent the particle or the probe from making contact with the particle or with the surface.

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Unless, again, if you look at this the other way, d equals F by k - for a given force if you want to minimize deflection then you increase the stiffness of the probe.

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If you want to operate in contact mode, which does give you extremely high forces so the data tend to be more reliable; but, you do not want to risk contact between the probe and the surface when you choose a high stiffness probe - in fact, all A F Ms that operate in contact mode do use high stiffness probe tip arrangements.

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Now, when you use an A F M in the contact mode there are again 2 methods in which it can be used: the first is what is known as constant force and the second is constant deflection.

As the name suggests, in one method of operation you maintain the force the same; in other words, you modulate the movement of the probe in order to get the same force between that you are measuring with your probe.

What that means is that you are not controlling the deflection; you can - in this constant force mode the deflections can be such that the probe does come in contact with the particle; now, that mode is okay to use when you do not have concerns about damaging either the probe or your sample **because of** contact that happens.

On the other hand, if you want to make sure that there is no contact - actual contact between the probe and the surface, when you use the constant deflection mode where you build in a feedback loop.

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So, based on this you have a loop that sends a signal to the cantilever and says 'I am experiencing high force move up' or 'I am experiencing low force move down'.

By constantly taking these feedback signals and adjusting the distance at which the probe is located above the surface you can essentially maintain a constant deflection of the surface. The primary advantage would be that you avoid actual physical contact between the probe and the disk and the surface.

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Now, when we talk about the non-contact mode where the probe is sufficiently far from the surface that the attraction is the predominant force - the problem with this is that the forces are weak; because, the farther you go away the forces are getting close to the zero value. So, you have to go back here and again look at this, if this becomes low then obviously you need a low stiffness cantilever in order to get a high signal from your measure[ment]- not to get a high deflection; because, what you are measuring is the deflection here.

Your objective should always be to maximize the deflection for a given set of conditions. So, you essentially tune your stiffness of the system in order to get maximum deflection for an applied force; but here, the forces are still weak enough that you are really not going to see significant deflections - the deflection magnitude is much greater in contact mode compared to non-contact mode.

So, how do you use than A F M in non-contact mode? You cannot simply rely on measuring deflection; so, the technique that is commonly used when we talk about the non-contact mode is to set this probe in oscillation.

Instead of holding it in place you let it oscillate at its resonant frequency; so, it is kind of sitting and oscillating sufficiently far from the surface and then the surface exerts the force - what is that going to do?

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It is going to change the resonant amplitude as well as the resonant frequency of the probe tip. So, in non-contact mode the primary measurements are classified into two: one is frequency modulation and the other is amplitude modulation.

In these techniques - in the frequency modulation what you do is you first set the probe in oscillation under at resonance conditions, bring it near the sample, and you look at the change in the frequency.

The change in frequency can then be related to the force that is exerted between the particle and the probe; similarly, in amplitude modulation you look at the change in the amplitude of the oscillation, which can again be related to the probe to surface force of interaction.

So, these two techniques are widely used; the frequency modulation technique is more sensitive and is mostly resorted to; the amplitude modulation is used in certain special cases. One of the risks with this non-contact mode operation is that there are situations where something called **snap-in** can happen, because it is an attractive force.

If you are not careful the probe will suddenly slam against the surface. This can happen when, for example, there are severe gradients in either composition or in the roughness profile; all of a sudden, if you have a spike in the surface that can cause this kind of snap in to happen; or, all of a sudden, you have a high surface energy material that the probe experiences - it will immediately get sucked to the surface; this snap-in is a problem, because it may lead to irrecoverable damage of the probe tip which would need to be replaced.

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So, in order to avoid that the analysts have come up with this procedure called intermittent contact or tapping mode, which is kind of a combination of the two. You do set the probe in oscillation, but you bring the probe sufficiently close to the surface that the oscillation can even extend into the repulsive region and in this case what happens is that you have essentially a continuum; depending on the position of the probe the oscillation will periodically put it in direct contact with the surface.

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Once in a while, the particle will make contact with the probe or the probe will make contact with the particle surface; but, the key difference is, in this case, you can set this stiffness high enough that it does not lock in - you can pull the probe back. The main problem in the non-contact mode is if because you are using low stiffness cantilevers there is no way that you can pull the probe tip back once it has locked into the surface; whereas, in the intermittent or tapping contact mode the stiffness values are high enough that you do have the ability to pull the tip back even after it has made contact with the surface.

These are the different modes of operation of an atomic force microscope. I am sure you have all seen pictures of surfaces that have been imaged using an atomic force microscope - the resolution is amazing, we can essentially get atomic scale resolution. In fact, when IBM came up with its scanning probe microscopy, you may recall, the way they advertise it or publicized it - they actually manipulated atoms using a probe to spell IBM; so, atomic level manipulation is possible with both atomic force microscopy and scanning probe microscopy.

Atomic force microscopes are much cheaper, much easier to use, require very little training; you just have to exercise care that is **probably** more important - it is not a very complex measurement to make. The drawbacks - so it has several advantages obviously over microscopic techniques - the biggest drawback is that with a scanning electron microscope you can look at fairly large areas at the same time - large, again, in a relative sense; you can look at millimeter square surface areas and still get good resolution. The atomic force microscope, because it is actually a contact probe measurement, you are really only looking at very fine regions at a time - you characterize micrometers at a time.

So, if you have a large surface and you try to characterize the entire surface using an atomic force microscope it will take you forever; so, the speed of analysis, the depth of field as we call it is much better for an electron microscope compared to an atomic force microscope; but, apart from that disadvantage there are many benefits to using atomic force microscope, so it remains a very popular surface characterization tool.

Now, the other technique that we should briefly touch upon is x-ray diffraction, and by the way there are entire textbooks on both these techniques $- A F M$ and $X R D$; so, if you are interested or you have a need to use these in your research you should **[lead/read]** them; there are also courses that are being offered in these subjects, I mean, there is a full 40 lecture course on A F M and on X R D.

If you really want to get into these techniques in depth you should spend a lot more time studying them - I am just giving you kind of overview of these techniques in this lecture. X-ray diffraction is used because most materials are crystalline in nature - something like 95 percent of naturally occurring materials and virtually 100 percent of man made materials are crystalline in nature.

What does that mean? What is crystalline? A crystalline structure is one in which you have a unit cell that has a certain characteristic and the structure of the entire material essentially replicates this unit cell in three-dimensions.

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So it is like, you know, if you can represent brick wall by simply looking at one brick that is exactly what crystallinity is; it essentially says that if you can identify a single unit cell which if duplicated in three-dimensions will produce the entire structure of the material, then you can call it a crystalline structure. One key thing to remember is these three-dimensions do not have to be orthogonal to each other, so that is one way in which it is different from the simple brick wall analogy.

X R D was invented in the 1920s actually and the key finding was that crystalline substance will reflect x-rays in a particular pattern called the di-fraction pattern; then there were three statements - the researchers name was Hull who essentially declared that - all materials have a diffraction pattern, he said each material has a distinctive difraction pattern, and the third statement he made which is very crucial is that if you have a mixture of various substances then the individual di-fraction patterns are still retained.

You do not get a mixing of di-fraction pattern from various elements or materials that are present. So, when you take these statements together what does it mean? The x-ray diffraction pattern of a material is like its fingerprint and just like a fingerprint for humans every material has a unique X R D pattern; so, if you can obtain the di-fraction pattern of any substance you can identify what it is - just like fingerprint analysis.

How do you make x-ray di-fraction happen? It happens naturally - if you take any substance and irradiate it with x-ray, then what is going to happen? It is going to setup an electromagnetic field; so, you have these electrons that are sitting around the atoms and they are all going to want to start vibrating in response to this electromagnetic field and as they do they start scattering as well as reflecting the x-rays.

Now, in an amorphous substance - which by the is the other extreme - in an amorphous substance you do not have a crystalline structure; you cannot predict the structure of the entire material by looking at a single unit cell; in an amorphous structure all these patterns of reflection and the di-fraction will cancel each other out statistically, but in a crystalline material because the atoms and therefore the electrons are arranged in a certain pattern it is possible to have constructive interference along certain paths even though you may be having destructive interference along a majority of the paths.

If you can measure the intensity along these preferential directions where there is constructive interference then it is possible to characterize the crystal lattice structure of the material; so, that is idea behind X R D very simply put.

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The way that it works is based on Bragg's law just like the A F M is based on Hooke's law and of course, Braggs law basically would state that - now, if you have two planes which are at distance d apart and you have x-ray coming in and getting reflected and let us say that this angle is some theta, so if you just extend these this angle will be 2 theta; this distance, actually if you look at it, will be d sin theta.

So, when 2 d sin theta equals lambda that is the wavelength or actually any multiple of lambda, then that is constructive interference.

This is, by the way, Bragg's law; so, for maximum intensity the angle and the distance of separation between the planes and lambda line up like this, so you want to calculate d you basically take n lambda by 2 sin theta and this distance of separation between any 2 adjacent crystalline planes gives you information regarding the crystalline structure of the material.

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That is a basic principle behind how this works; now, what you do is you keep changing the angle theta and you plot 2 theta versus intensity and you get a certain characteristic spectrum for every material - you have certain peaks and so on. This spectrum is what is unique to every substance; so, by matching this against a material that you have in your reference library, you can actually identify what this crystalline material is.

Now, there are a lot of - in addition to looking at crystalline structure X R D spectra can also be used for other purposes; for example, the extent of crystallinity or the degree of crystallinity is indicated by the sharpness of the peak; so, a highly crystalline material will have very sharp and well defined peaks, whereas an amorphous material will have a series of overlapping signals. The size of the particle - the crystalline size - can also be indicated by the width of the peaks; as you keep making the particle finer and finer this

width will change and the peaks will not only become as it becomes more crystalline the peaks will get taller.

As you make the particle size finer and finer you will also see a broadening of this peak. So, the width as well as the height of the peak give you a lot of useful information about the crystallinity of the material as well as the size of the material, and also the specific dependence of intensity; 2 theta is a function of the material itself the - chemical composition of the material; for example, alumina will have a very different X R D signal compared to, let us say, silica.

If you want to distinguish between two essentially crystalline materials - alumina and silica, you can do that by using $X \cap R$ D or if you are just looking at the chemical composition you can also use other methods such as SEM, EDX and so on.

But, just like $A \nvert F M$ the big advantage of the $X \nvert R D$ is that it is relatively easy to use and it does not again require the extreme conditions that an SEM or a TEM would and the data can be obtained very quickly; the limitation of the method is again very similar to the $A \, F \, M$ - you are really probing extremely localized surfaces, so your field of vision is much smaller in an X R D compared to some of the other techniques that we have been talking about.

X R D is predominantly used in qualitative mode for doing qualitative characterization of the crystal structure of a material; A F M on the other hand can be used very effectively in a quantitative mode, but that is another thing that distinguishes an atomic force microscope from the microscopic techniques we have discussed earlier as well as the X R D technique.

These are essentially qualitative characterization techniques and therefore they provide a certain type of data; now, as a process engineer quantitative data is mostly more valuable to you then qualitative data because the qualitative data typically does not change once the process has been established or once the material has been developed, what changes is are the more quantifiable parameters.

A F M is very gainfully used as a line monitor; for example, if you are let us say, you are manufacturing or synthesizing a crystalline material and you want to make sure that the process is under control, then an SEM/TEM is not the right tool to use. $\overline{X} \overline{R} \overline{D}$ may be \overline{X} R D is probably a good tool to use if you are primarily concerned about the crystallinity of the material.

But, if you really want to know whether the process is under control the simplest technique to use that will give you a variety of information is A F M; because, it is gives you not only the structure of the material but it also tells you something about the morphology of the material, the three-dimensional topology, tells you something about the roughness of the surface.

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It is a very power full tool that can give many types of data that are useful for a particulate process and so is X R D. Again, if you look in literature on particle characterization, especially again, as you go to the nano sizes you will see that the literature is dominated by results obtained using these two instruments X R D and A F M.

These are techniques that are absolutely vital if you want to get in to nanotechnology; it is a good lead in to what we are going to talk about in the next module of this lecture, which is nano particle characterization.

All the techniques at we have discussed so far do have applicability to nano particles but they must be customized for the application you have to use them differently when you are trying to characterize nano particles compare to other types of particles.

Starting in the next lecture we will spend some time talking about nanotechnology in general. There is a lot of confusion about what is nanotechnology, what is nano; so, briefly describe the characteristics of nano particles, briefly talk about methods of synthesizing nano particles and then we will focus on characterizing the structure of nano particles as well as the dispersion characteristics; we will talk about nanotechnology one of the key challenges is after you make the nano particles how do you keep them as nano particles and how do you prevent them from coagulating or agglomerating and turning into micron size particles.

So, there are lot of interesting aspects of nano particles synthesis, dispersion and characterization that we will deal with in more detail in the next few lectures. Any questions on what we discussed today? See you at the next lecture then.