Symmetry and Structure in the Solid State
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Lecture - 56
Powder Diffraction 1

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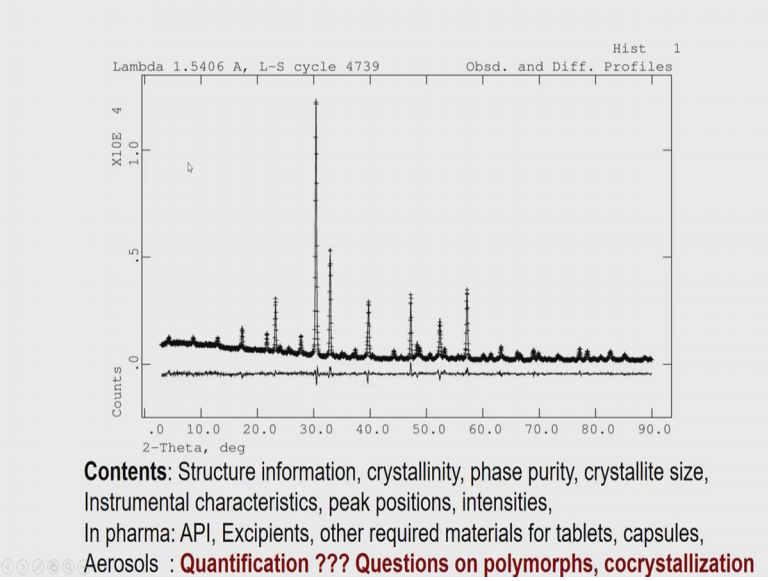

As we have been discussing the x axis contains all the information that is required of the geometry of the diffraction and the y axis contains all the information about the structural aspects. We see a typical pattern XRD pattern which is shown here, where we we have marked the possible peak associated with these; and the dashed lines here are the ones which are calculated structure factors. We will see how calculated intensities, we will see how it comes up.

And then the one below here shows the difference between the observed and the calculated, essentially helping us to determine the structure of this material, by the so called read filled assignment. So, in the next maybe half an hour or 1 hour, we will try to cover all aspects related to this powder diffraction techniques, because this is something which is quite a relevant in industry and also it is quite a relevant in teaching modules.

And at the same time of course we do not forget about the symmetry that we have and we can associate with powder diffraction patterns. So, the questions which we can answer, in fact, by just a record of I versus 2 theta on a powder sample we discussed yesterday the three modes of data collection.

So, let us say that this is a typical standard X ray data, which is coming from the reflection mode. So, we take this pattern and the what are the contents of this pattern? The contents of this pattern or it contains information about the structure. It also tells us about the crystallinity. If you look at the background associated with this recorded pattern; you see the background is slightly falling, but essentially remaining more or less a constant.

The more the constant it is as we go to higher angles it suggest that we have a very crystalline material because, the peaks are quite sharp and the width of the peaks are not so very different from each other. They are normally about the same size. In fact the techniques of analyzing the peak widths and so on also gives us several other information associated with it; apart from crystalinity the other aspect is one once we have a compound like this we can also question the and answer the phase purity questions, pure sample will have an unique powder diffraction patterns.

So, powder diffraction pattern is almost the fingerprint of a given material. So, that way the presence of the databases the in organic crystal structure database, they came re structure database it has all the data sets associated with single crystalline structures. On the other hand ICDD database, the international centre for diffraction data has information and all the powder diffraction data which has been collected over the years.

So, very closely related compounds will resemble each other as far as powder diffraction is concerned, if you have just done for example, some changes in the alloying conditions or some changes in materials. Or if you have made some changes by substitutions by changing one atom to the other and so on. The powder diffraction pattern will not be very different, but it will be different from each other I said because it is the finger print of the given material.

So, phase purity is one possibility which we can analyze, more than one phase also can be analyzed doing a powder diffraction analysis we will see as we go later. And we can also determine the size of the crystallite by measuring the full width at half maximum, that is what is known as a Scherrer formula which will give us that information. We of course, have to worry about the instrument characteristics we discussed already the modes of data collection in the previous class, but apart from that we they depending on the instrument the width and the the so called asymmetry associated with the peak,

because the peaks may not be exactly symmetric as we see in this example I have given here.

It may become asymmetric and that probably is due to the way in which we collect the data. So, the instrument characteristics also play a very crucial role. The peak positions and the intensities of course, we already said that peak positions are the geometry the intensity has the structure.

So, when we come to pharmaceuticals particularly the questions come about the as active pharmaceutical ingredient, one once they make this compound ready they would like to ask what is the characteristics of this API? Whether this particular API is identical to the API which has been marketed by someone else or this particular API has the issue of what we call as a polymorphism which means that it may have a different crystal structure.

So, questions on polymorphs cocrystallization which would mean the formation of co crystals the formation of salts the formation of eutectic those kind of phases, will also come into the picture. We can also work out in the case of tablets, we can analyze the tablets directly other required materials for tablets apart from excipients and the API and then we can also analyze the capsules and aerosols.

So, these are some of the advantages with powder diffraction which probably we will not have with single crystal diffraction; other than that of course, all the information that is contained in a single crystal diffraction is available in this one dimensional profile of the powder. So, in some way or the other there is one dimension profile has to be broken down into three dimensional reciprocal lattice information. One once we do that we can determine the structures even by using the single crystal approach.

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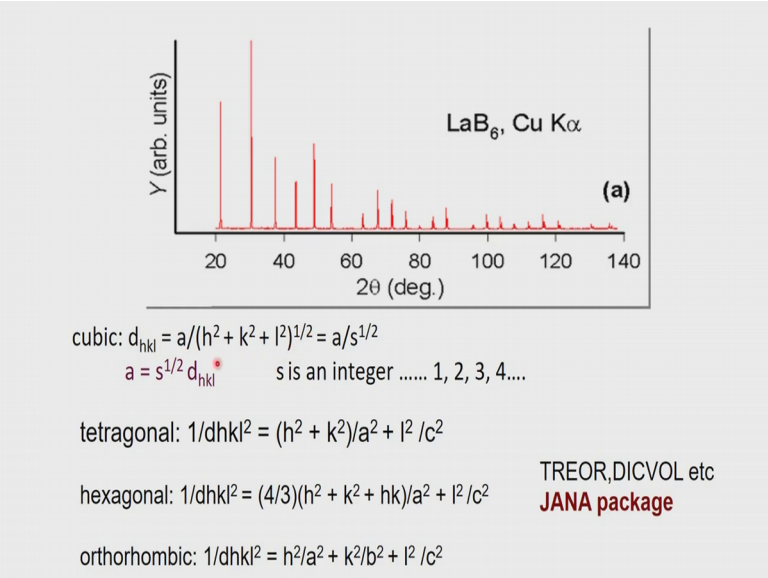

So, this is the basis of it. So, we will now go systematically to how we index a given pattern. LaB 6 is the standard compound which is supplied by many of the companies. They give us routinely this compound and its uses copper K alpha radiation with this; this is the diagram. This is the diffractogram we will get; always call this as the diffractogram or X ray pattern do not ever call these as a X ray spectra.

Because X ray spectra means something else anything to do with spectrum or a spectra means something very different; because what it means is that you have a ground state of the material and it is taken to a higher excited state. And then there is a there is a radiation which is emitted from the excited state to go back to the ground state, because it cannot stay in the excited state forever.

There is a time lag in that particular period or in which it comes down to the original ground state. And when that happens whatever comes out as a radiation is the spectra which contributes to the spectroscopy. So, all spectroscopy is therefore, have a time component associated with them. And therefore, we can straight away do Fourier transformations in spectra, because with the time component is built in there in diffraction we cannot do the straight forward Fourier transform unless we solve the phase problem.

The phase problem is overcome in case of spectra so; the important point to remember here is that this is not spectra, it is essentially the scattering that occurs we have

discussed enough of the scattering over the days. So, it is not spectroscopy which is involved. So, what we should therefore, always say the as a diffraction pattern or a diffraction diffractogram and X ray spectra is result for some other phenomena which can also be done then can do X ray spectroscopy, different kinds of X ray spectroscopy is using electron beams and so on.

So, depending upon the crystal system, we have already seen this table sometime ago the value of d of hkl can be calculated depending upon the nature of the crystalline material, that is whether it is a orthorhombic crystal or a hexagonal, tetragonal cubic of course, monoclinic and triclinic will have more complex expressions. So, in the case of a cubic system it is fairly straight forward calculation.

So, suppose let us say the given diffractogram belongs to the cubic system, we will be go through a very quick process of how we go and ahead and index that cubic picture.

So, d of hkl is a which is the scull dimension divided by h square plus k square plus l square to the power of half. Now this quantity hks plus k square plus l square we can write it as s and that has to be always an integer because hk all or integers. So, the h square plus k square plus l square should also be an integer. So, it can take values 1 2 3 4 etcetera.

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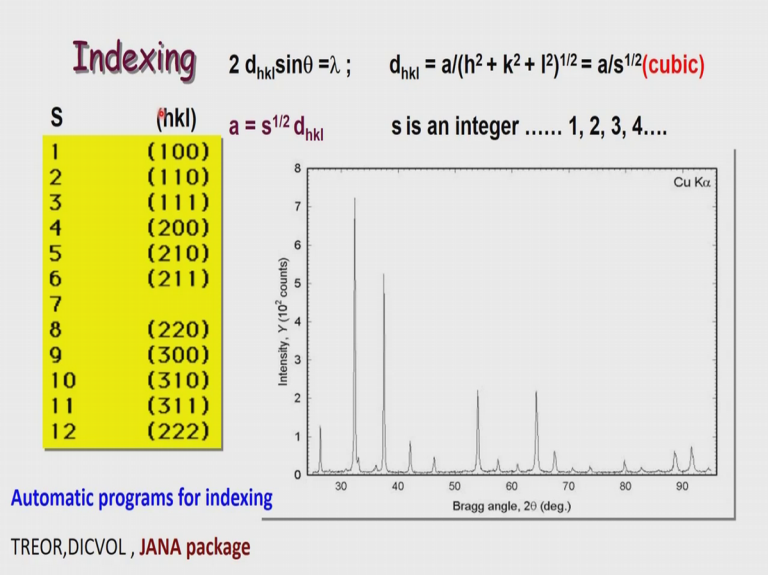

So, let us take a situation where we use this let us take this example which is given here this is the intensity versus 2 theta. So, we take this example to show how the indexing process is done. So, what we do is we can we have of course, 2 d sin theta lambda from which we can write the hkl in this particular form, where S is the value of h square plus k square plus l square. We say S can take the various values, so the values of S can be 1 2 3 4 5 6 as it written here and then we assign the hk possible hkl planes in a cubic system. Remember in a cubic system a equals b equals c alpha beta gamma are 90 degrees.

So, whether it 1 0 0 or 0 1 0 or 0 0 1 it is the same. So, this is the associated multiplicity because of the symmetry. So, again you see symmetry is the dominant factor in any diffraction experiment even in the case of powder diffraction. So, when S is equal to 1 the only value we can assign to hkl is 1 0 0. So, when it is 2; the only value we can assign is 1 1 0 because h square plus k square plus l square has to be S and that has to be an integer.

So, 3 4 5 6 therefore, has well defined hkl values. So, we can therefore, assign hkl values to the peaks which we find in the diffractogram. So, the values of the hkls can easily be identified in a cubic system, by just giving the value of S and giving each and every peak the corresponding value of S; S is 1 2 3 4 5 6 and you see that there is no way we can assign 7, because h square plus k square plus l square if we take three integers it will not add up to 7 so, 7 is forbidden.

So, as a consequence we now have uniquely indexable pattern and so, we get these hkl values; one once we have these hkl values we can calculate d of hkl and one once we have d of hkl we can get to the a of hkl; because d of hkl can also come from one say d is equal to lambda by 2 sin theta. So, we can get the d hkl value which is lambda by 2 sin theta from the 2 theta value here; we calculate the sin theta value and lambda by 2 sin theta will be the d of hkl and this is equal to a divided by h square, plus k square plus l square.

We have the hkl assigned here. And therefore, we can get to the value of a which is what we want because we want to find out the cell dimensions of the given crystal. So, this is the easiest example with which we can illustrate ah, but normally there are lots of programs which are available in in opens webs; websites and these are all automatic programs for indexing. The logic in which it goes is that any given pattern is considered

to start with is a cubic system, the one of the requirements that it should have is that it has to satisfy this conditions of the integers being there for we are associated with it. So, if we cannot assign the peaks which come in the diffractogram to these values of S then we know it is not a cubic system.

So, slowly we go up in the reduction of symmetry so we reduce the symmetry to tetragonal, hexagonal, trigonal, orthorhombic, monoclinic and triclinic. In that process we get evaluation of how well the pattern is fitting the assigned hkl values. And as a consequence we get to the cell dimensions and then we look at the possibility of identifying a unique cell dimension that can be indexed.

So, this process is known as a indexing and this is now very automatically done in many programs and the standard programs that are generally used are they TREOR, which essentially means TREOR trial and trial error is what is it trial and error method. Trial and error method and we also have the compound program called DICVOL we have several other programs there is a package called criss fire which is available.

But apparently of late the criss fire has some problems. So, you have to be careful when you download criss fire because criss fire used to work on earlier operating systems, the current a improvements in technology in computer science and also the incorporation of now the modern day memory boards, will not allow criss fire the old one to run. But then there are other programs the best package that can be used for every purpose starting from indexing the powder diffraction to structure solution is the JANA and this package again downloadable free and this can be accessed through the web.

So, these are the programs which will automatically index a given pattern. So, whatever be the crystal system in principle following this methodology roughly, which we mentioned we can determine the unit cell dimensions. Having determine the unit cell dimensions what are the questions we come across in X ray we already discussed what is the content of a the x r department in a in the powder x r department. So, I thought I will sort of highlight the uses that are relevant in pharmaceutical industry and also we general it should be chemistry.

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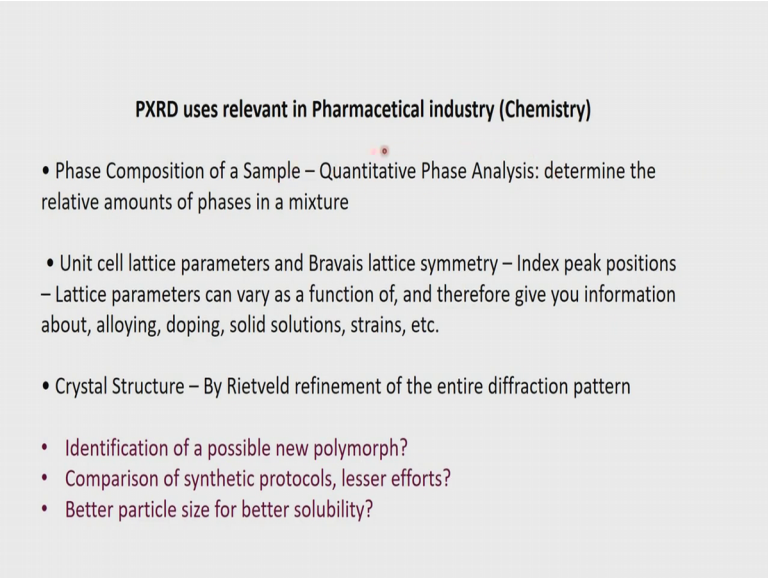

So, one is the phase composition of a sample this is very critical particularly if you want to generate a new pharmaceutical material. So, we therefore, do a quantitative phase analysis which is possible to determine the relative amounts of phases in the mixture. So, suppose we have a mixture of phase one and phase two both of them will be inside this particular diffractogram and as I mentioned that, each and every material is like having a fingerprint associated and that is the powder diffraction pattern. So, if you have two different compounds mixed into a system the two different compounds will give two different types of XRD patterns.

By type I mean even the full width at half of maximum will be different the shape of the peak will be different and so on. So, effectively the profile of the peak which comes in a diffraction experiment is characteristic of the material. And therefore, if you do the analysis of the profile in principle we should be able to find out the possibility of more than one phase being present in a sample.

So, the way in which we go about is we determine the unit cell parameters and of course, Bravais lattice symmetry index peak positions and lattice parameters can vary as a function and therefore, give you information about alloying doping solid solutions strains etcetera these are all very critical in pharma industry.

The other most important aspect is since we say the profile is characteristic of the material and its profile fitting is a issue which we can sort out in order to get the all these

issues completely analyzed. One can also determine the crystal structure by what is known as a Rietveld refinement, which about which will spend a few minutes as we go along. And this is the refinement of the entire diffraction pattern see whether we when we make an analysis and identify a phase, and then we want to doubly verify that it is a single phase. The best approach is to be always use the whole pattern the complete pattern rather than use patches of with this reflection that reflection and so on.

Remember when we did the indexing with read out the peak positions we did not bother so, much about the way in which the peak is appearing the shape of the profile and so on.

But it is important that we use the shape of the profile because the shape of the profile is definitely represents the integrated intensities. So, it is a integrated intensity we will need in order to calculate in order to determine the structure, because we already know that structure is along the y axis of the powder diffractogram. And therefore, we have to analyze these profiles extremely carefully after indexing those patterns, it is not necessary that we have to index only some 10 or 12 reflections we have to, in fact in principle indeed a index the entire diffraction pattern.

Some of the peaks maybe weak some of them may be strong and we have to identify all possible peaks which appear one once we have the crystal system which has been analyzed. So, these are some of the issues which are essential for pharma industries and this is where careful analysis has to be done particularly when we are looking at the identification of possible new polymorphs or comparison of synthetic protocols, lesser efforts may be you know you have a two step procedure to make a API.

Somebody else as I tensed a procedure to make an API, but have we really made that API. So, such questions come up and the better of course, the other issue is better particle size for better solubility; solubility is a major issue. In case of pharmaceutical materials particularly most of the pharmaceutical materials are delivered or administered in solid form. And therefore, the powder diffraction of these materials becomes very very crucial.

So, this is a very basic technique that has to be employed in pharma industry in order to characterize the solid pharmaceutical materials. So, what are the accesses the access points which we are which we have got to do this kind of an analysis? Of course, we can always record a powder XRD of a given material is very easy procedure now, it is not like you know we spend a lot of time to grow a single crystal and get the single crystal

diffractometer powder is already formed in our experimental protocol. But is this powder a pure powder is this powder a crystalline powder, how crystalline is the powder how much of non crystalinity is associated with this powder or is the powder amorphous? These are all questions which come and when we want to answer those questions there are certain plus points which are available already.

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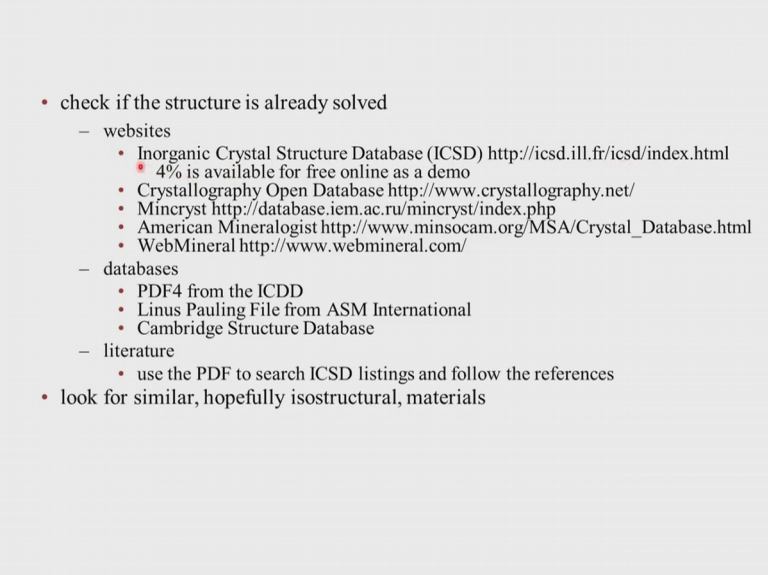

So, first thing is we have to check if you want to determine this structure check if the structure is already solved. So, there are several websites which are going to help you out one is the Inorganic Crystal Structure Database ICSD the web address of which I have given. And in fact, four percent of this is available for free online as a demo. So, one can use that and get an inc link of how to use the ICSD. And then it can be put on order crystallography open database which is available in this website where you can get some information or if not all about the structure.

Mincryst which is having this website information, we can also go there and get to the datas. American mineralogist is a another source where we have all the datas on minerals which have been and in fact, the classification is also available among the minerals if one goes to that site. The web mineral again is a another sub set of American mineral it just a kind of thing and there again we can get information on the minerals; other than that we have the databases as I already mentioned the international centre for diffraction data is the one and the most for most available ICDD package, which will be using a program

where the package called PDF 4, which can be bought at a cost. And then of course, we have the Linus Pauling File for ASM International. It is actually a sub sector of sub section of ICDD.

The best is to of course, access ICDD because that is the one which has all the possible data collected so far on the surface of the earth ah. In fact, they have some data sets collected in space as well on some powder data. So, they have everything in stored and it is easy to access the ICDD database. And of course the if you want the single crystal data and then ICDD is also linked to the CSD now.

So, you can link these two get all the date of both the powder as well as the single crystal information. You get information on what is called the crystallographic information file which we discussed when we discuss the structure determination in the powder in the single crystal case. So, we also have the availability of a Cambridge structure database.

The literature of course, we can always go to literature in the end earlier days it was the only available source, but now people go to literature only after they do not find anything in these; the way in which now modern day science done is go to the website. In fact, a way in which anything has to be done is go to the website you want to know how to make sambar? You go to the website you do not do it the way we used to do it earlier days. So, we first go to the website get all the ingredients and follow the protocol. So, website is the become a part and parcel of our life. So, we go to the websites get whatever information we want.

So, website therefore, have the information you want for all crystallographic data as well. Then of course, the databases these are storage places where you store all the data which is available, it is like your brain you have you store the data. So, what you learnt in class three, in general you should be able to recollect when you are reminded of it, but when you do not have to be reminded of what movie you saw when you are a 10 year old? The moment you are activated you will remember it. So, it depends upon what kind of databases we can access, but databases are in the necessity to get to this. And the last result happens to be literature still remember when we went to when we were doing our PhD studies way back in the 70s none of the top two were available and so, we have to go only to literature.

I still remember going to the library and climbing up the stacks and removing the dust of the old books and then, take it the old journals and see whether the relevant literature is available there or not. It was quite a painstaking methodology which we used to use. So, normally when we go to the library we will be coming out very tired and hungry, because we will be climbing up the ladder to access the books which was stored way up there; and then taking it out and opening it closing it with removing all the dust again go up come down. And each access point will be a different parts of the library and depends on the size of the library you are accessing it would be quite a painstaking exercise anyhow.

So, the we can use the PDF to search ICSD listings and follow the references. So, ICSD also helps you to ICSD and also ICDD both they help to follow the references because they give a list of references. This will help you in looking for isostructural materials similar structures isomorphs, isostructural those materials can be accessed. So, this is the access point which we have and therefore, powder diffraction is not just a standalone recording of the pxrd, it now has a lot of information that is hidden in it which we can isolate and identify.

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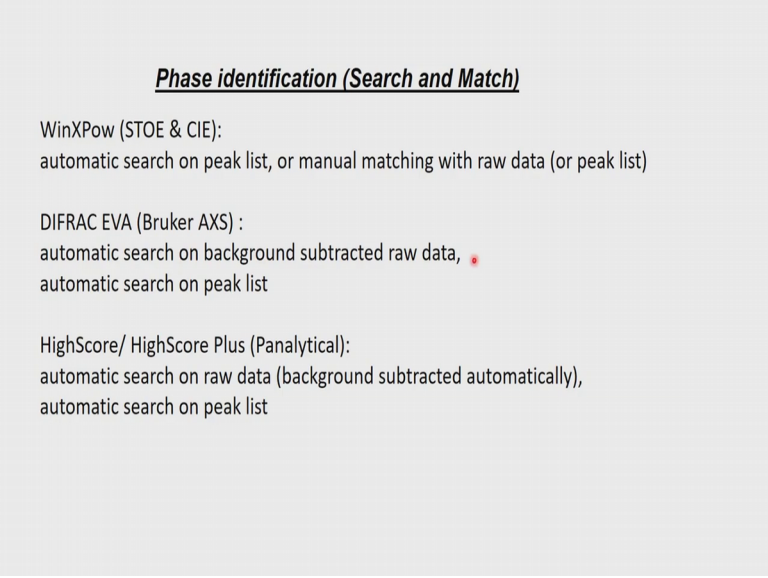

So, there is the main important thing which comes up in a pharmaceutical industry is the phase identification the so called search and match. So, we there are packages that are available we associated with the machines which we use. So, the diffractometers which

you use if you use STOE and CIE you have a automatic search on peak list or manual matching with raw data or the peak list.

If you lose Bruker you have this package called DIFRAC EVA which is gives you access to automatic search on the background sub subtracted raw data automatic searches, peak list and so on. The most recently developed package which is the high score plus by Panalytical allows for automatic search of raw data background subtracted automatically and also it allows for the search of the peak list. So, all these increments now come with the facility that you had you cannot you do not have to worry too much, you just ask the machine or the computer which is connected to this diffractometers to do the phase identification it gets automatically done.

It not only searches for the required phase, it also matches the phase with the databases. And so we now get a very clear idea of a whether we have made a new compound or not.

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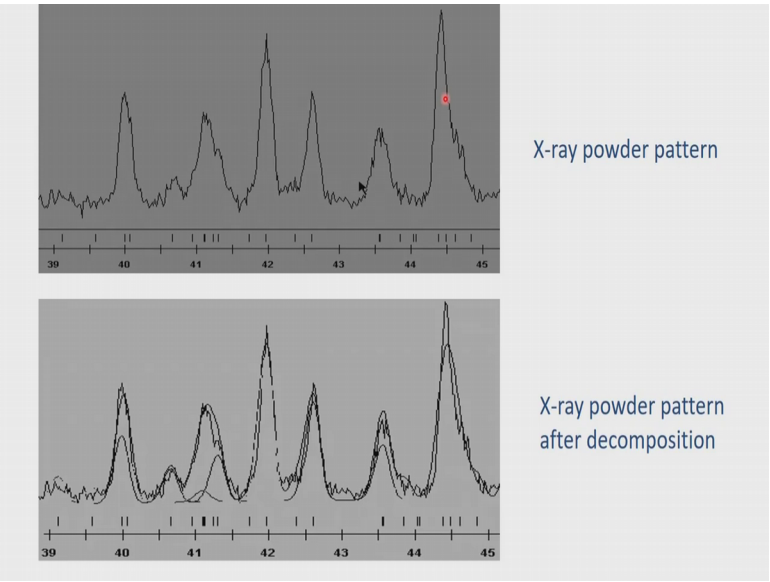

Now, here is a situation where we now jump on to the determination of the structure, see the number of peaks that are produced in a diffraction experiment, whether it is a powder diffraction experiment or a single crystal experiment, are limited to the number of access points we have on the limiting sphere the reciprocal that is information. So; that means, that all the reflections that we can collect on a single crystal should also be possibly collected in a powder, depends upon the what range of 2 theta we are covering.

And so, if you have a pattern like this particular pattern you see is if you expand the region from 39 I hope you are able to see it 39 to 45. If you expand that region of the powder diffraction pattern you will see not very comfortably shaped peaks, but a real distribution of peaks in this region. What one can do is one once you have index the pattern you know the crystal system, it is not generally possible in a straight forward way to determine also the space group unless of course, you do a search match and find out the corresponding crystal system in the database. Otherwise you only have the crystal system.

Now, one once we have the crystal system identified a b c alpha beta gamma identified for the given compound, then you can calculate how many hkl values are possible and where they can appear in 2 theta. Use the Braggs equation. So, when you do that you will mark the ones which are marked as horizontal the vertical lines here, are the ones which actually tell you what are all the peaks that can form; if you look at region like this you see that there is a severe overlap of one or two peaks could be 2 peaks, 4 peaks, 6 peaks and so on.

This is the problem in analyzing the X-ray powder pattern. X-ray powder pattern is as we see it is a one dimensional profile which is extending our the 2 theta range. And therefore, the individual reflections now may appear under one peak may appear under several individual peaks may appear one under one peak. So, this is the peak overlap problem unless we solve this peak overlap problem we cannot get the intensity is of individual hkl planes. So, to do that there is a procedure called the pattern decomposition.

So, this is a illustration of how one can do this? I am not going into the detail of how it is done because of lack of time I think we are almost coming to the last couple of hours of the entire length of the course. So, we cannot just spend time on that, but essentially I will tell you how the breakup is done? The breakup is done by actually trying to develop the shape of the profile. So, we do what is known as a profile analysis.

So, the shape of the profile now will be able to be fitted under this particular curve. So, this is essentially a curve which is going from 39 to 45 and under that each and every position of hkl is associated with the peak. The shape of the peak how we assign I will tell you in a minute where that is referred to as the profile refinement protocol. So, we

therefore, now what we do is we distribute the peak positions for example, under this position which you have here, let us take an example this one particular this peak for example, at 42 it is a unique peak there is only peak. So, we cannot see that the peak can be fitted with a function which goes under it the width of the peak and the shape function associated with the peak can be generated mathematically.

And how we do that? We will discuss in a minute; so we therefore, see when there is a severe overlap, there are large number of peaks for example, in this region if you consider there is a peak here 1, there is another peak 2, another peak 3, another peak 4. So, all these four peaks together will give rise to this profile which you have got in your recorded pattern. So, the recorded pattern why it was looking so funny is because it has it is made up of four reflections. So, when once we identify those four reflections, we can attach individual intensities to that and adjust the intensities in such way that we mimic the observed pattern.

So, we have the calculated intensities the shape of the profile is evaluated, then you mimic the shape of this; one once you mimic the shape of this you know now you have fitted the profile. And this process is known as profile fitting and we can refine this profile with respect to various parameters, which are used to describe this function profile function and therefore, we can do a profile refinement and when a good refinement occurs we know that whatever cell dimensions we determine for the structure is very very accurate. So, it is not enough just to index the pattern and say this is our compound, we have to also do your profile refinement to verify the indexed pattern.

And then get the information on individual peaks see. So, far we have not brought the idea of structure, we are not telling where the atoms are and how the atoms are located we are just trying to fit the profile and therefore, this process is known as profile fitting which will give you an evaluation of the geometry of the situation. If you want to put in the intensity information that is a different story which we will see and that is the one which takes us to the Rietveld refinement protocol.

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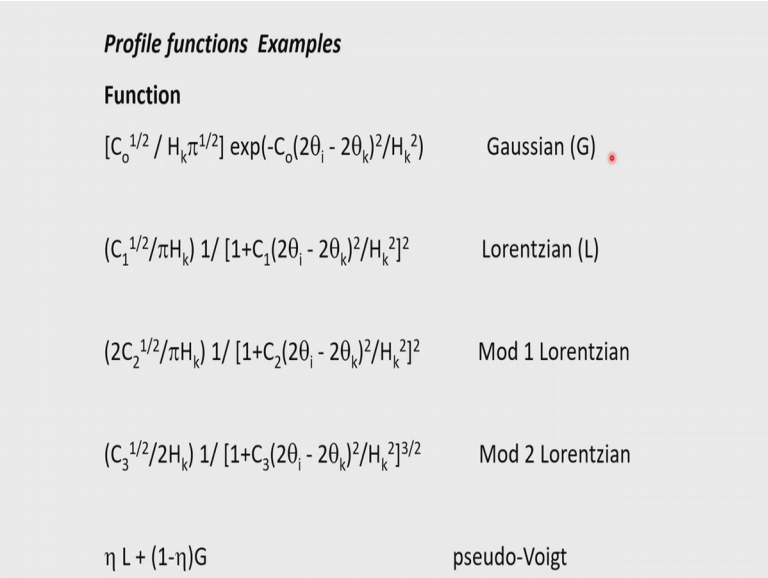

So, let us go further and we see here the types of profile functions we can fit. So, we have to get a function which is looking like this right. So, we have to get a function which will look like that then let us take this function this is the profile so associated with this reflection.

So, in order to get that profile function we need to have several parameters and those parameter are supplied mathematically by these following functions. One can use a Gaussian function if one is collecting neutron data, the peaks coming out from a neutron diffraction will always be Gaussian in shape. The reason is obvious because the diffraction is not from the electron density around, but it is from the nucleus. And therefore, the size of the nucleus is about 10 to the power of 12 centimeters minus 12 centimeters and the size of the atom size is about 10 to the minus 8 centimeter. So, its 4 out of some magnitude smaller and the incoming radiation is X ray and incoming radiation is also one extra.

And therefore, we shape of the profile is generally a Gaussian in other words the atom positions are now very accurately available through the location of the nucleus and therefore, they all become individually delta function. So, the Fourier transform of the delta function will be a Gaussian or vice versa. So, we therefore, have Gaussian functions, very easily fitting neutron data. So, it is recommended that when we have a accessibility to a neutron source powder diffraction data of a neutron is very very useful.

In fact, a powder diffraction data can also help us in finding one once we solve the structure we can also find the hydrogen atom positions. The only problem is that the neutrons are very very even though they are moderated from a nuclear reactor; they are very very strong.

And therefore, the amount of depth powder that is required is quite a large amount, we need gram quantities of the material to do neutron diffraction by powder; where as you can you need only a few milligram sometimes even a 5 to 10 milligrams you can get a very good X ray diffraction data. So, this is the limiting you see the two techniques go hand in hand. The technique of neutron diffraction by itself is not a standalone even though one could say that one can make it a standalone technique, depending on the particular compound which is designed for neutron diffraction.

Otherwise it just goes as a hand in hand in glow technique associated with X ray. So, X ray technique is the paramount it is the first one which is supreme, the only issue about X ray is as we know is the falling of the atomic scattering factor which sin theta by lambda which does not happen with neutrons. So, even though in the syllabus I mentioned we will discuss neutron diffraction it looks like that we are running short of time. So, whenever possible I will bring in the advantages and did disadvantage of using neutron.

And at the same time mention a how superior the data from a neutron would be for determining the hydrogen position, because there is no variation of sin theta by lambda fall of this scattering factors. There is what is known as a scattering length which is characteristic of the given element and this value can be both plus and minus we can normalize it to 1. So, it is be either plus 1 or minus 1 and the range of these values can be occupied by various elements.

But these elements now will not show any change with respect to sin theta by lambda. So, it remains the same value throughout the range of the data collection. The other possible fits which are given there are we have given four of them it depends on the instrument on which you are collecting the powder data you are. So, if you are using a Lorentzian data; Lorentzian function you use these parameters, I am not going in to tell you what are these parameters except to tell you that, if you take this as the initial position of theta; and this is the final position of theta. The difference between these is

sort of minimized with respect to these functions the C 1 and C 2 constants will adjust the functional parameters.

So, we have Lorentzian type in a module Mod 1 Lorentzian, Mod 2 Lorentzian and very often we use this so, called pseudo-Voigt function. I am not explaining individual values, we have used for example, here H associated with this and we have used G associated with it these are all functions which are readily available ah. So, these functions are already available in all the instruments. So, so in instrument determined; the instrument determines the profile function which we normally adopt. So, for a routine powder diffractogram where we get from the machines like panalytical or Bruker we normally use a pseudo-Voigt function for the profile fit, just remember that I do not think is very particularly important.