X-Ray Crystallography
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Lecture - 22
Qualitative Phase Analysis

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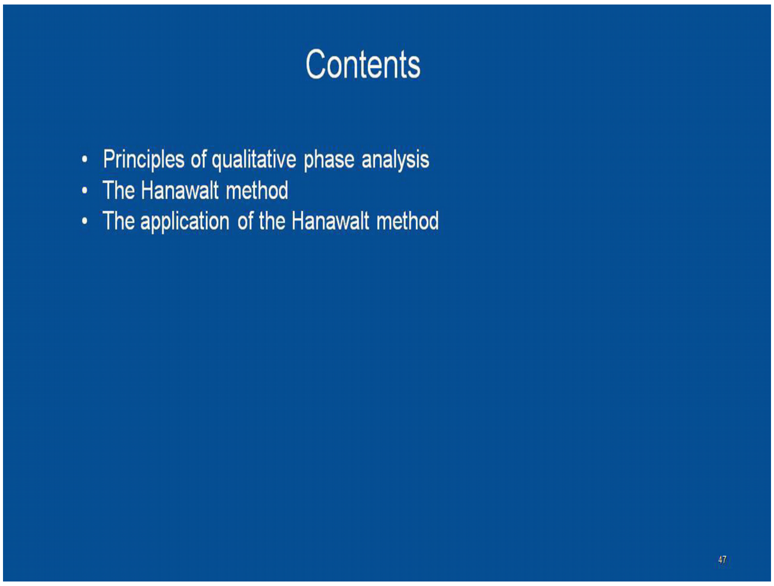

Contents

- Principles of qualitative phase analysis
- The Hanawalt method
- The application of the Hanawalt method

X-ray diffraction has many different applications. An important application of X-ray diffraction is Phase Analysis.

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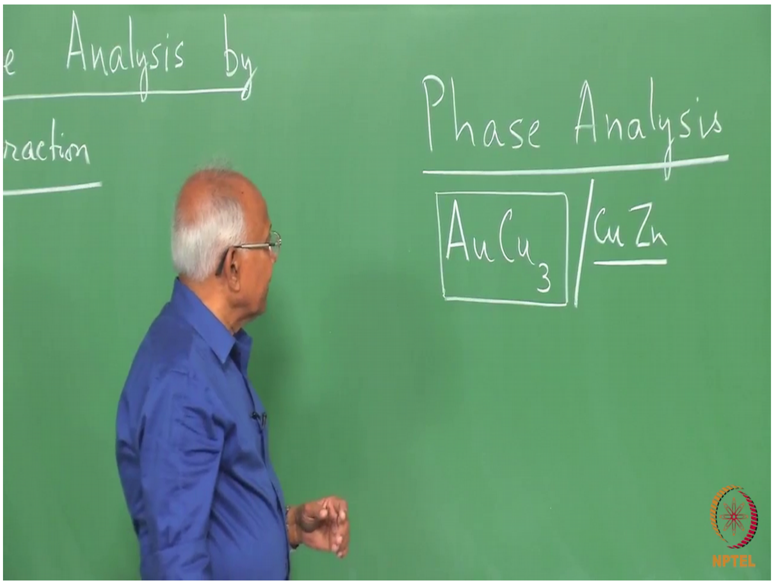

Now, phase analysis is quite different from elemental, chemical analysis. Say for example, if we have a compound say Au Cu 3 or Cu Zn or anything. This is a single phase although made up of two components: one is gold, the other is copper. Similarly when we talk about Cu Zn it is a single phase made up of the elements copper and zinc. Normal chemical analysis constitutes the technique to find out how much of each element is present in a particular phase or in a particular element. But when we talk about the phase analysis it is not elemental chemical analysis we talk about the individual phases.

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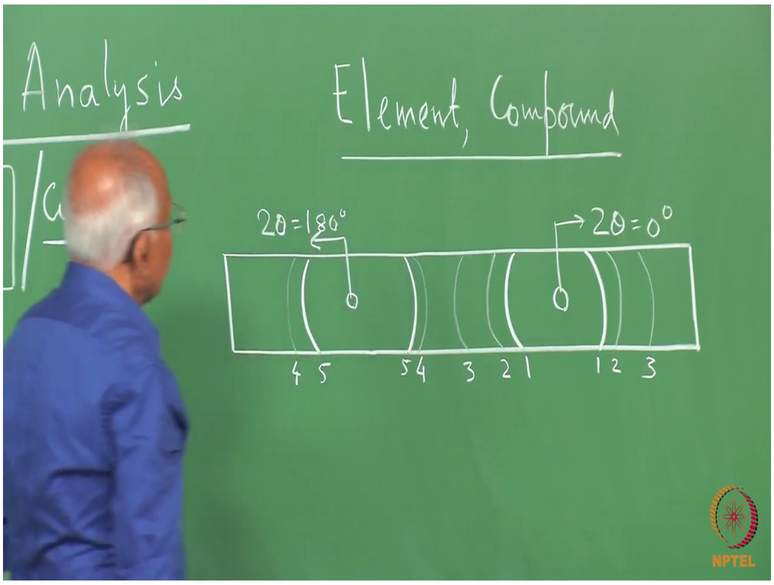

Now it so happens that any phase made up of an element or a compound of several elements. If we have a phase made up of a single element or a compound of many different elements, then X-ray diffraction from that phase will yield a unique diffraction pattern. So, what we mean by a diffraction pattern? The diffraction pattern taken from a particular phase will have a number of diffraction lines at definite theta values.

Say for example, this is the diffraction pattern taken from a particular phase. Now the diffraction pattern consists of a number of lines 1 1, 2 2, 3 3, 4 4, 5 5, etcetera; and these are positioned at particular theta values. And these are positioned at particular theta values. Over and above that these diffraction lines have different relative intensity values. Say for example, the line 1 1 has a very strong intensity, like 5 5 also have the strong intensity. Line 2 2 has a somewhat less intensity, 3 3 and 4 4 have even less intensity.

Now, when we talk about a diffraction pattern we talk about 2 things at the same time: the location of the lines at particular theta values, and they are relative intensity.

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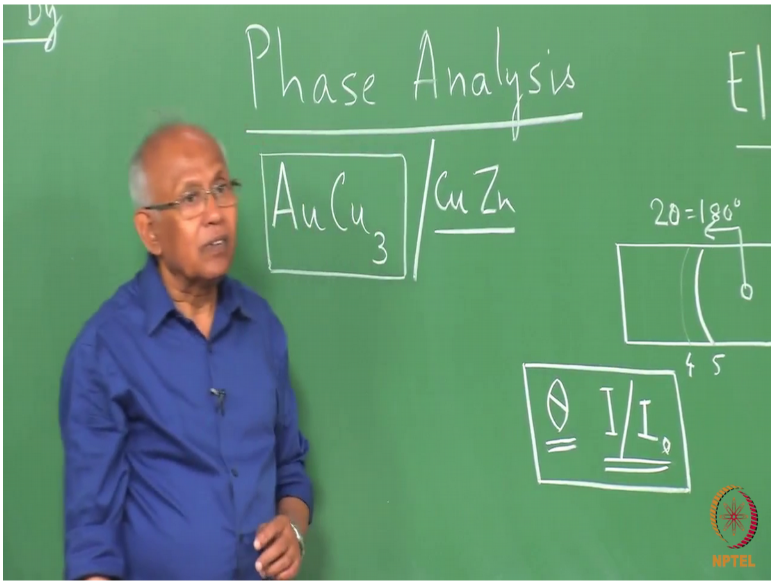

So, relative intensity of the diffraction lines is also very very important. Say if I 0 is the intensity of the strongest line in the pattern then the relative intensity of a line can be found out by taking the ratio I by I 0; where I stands for the intensity of a particular line. So, when we talk about the powder diffraction pattern from a phase it may be an element, it may be a compound, then both the things are very important to note.

So, you must find out where the diffraction lines form, at what theta values, and what are the relative intensities of the lines? Now this diffraction pattern is very unique for a particular phase whether at element or a compound. Say for example, we have got this diffraction pattern from an element or a phase A. Now if we find out the diffraction pattern for another phase or element B, then these 2 will be quite different. In fact, just as by recording the fingerprint from 2 different persons they can be distinguished, because each person has a definite type of fingerprint which is unique to that person alone.

Similarly, the diffraction patterns taken from two elements A and B or 2 phases A and B are also very unique to the corresponding materials. The diffraction pattern from two different elements or two different phases cannot be the same. A and when we talk about the pattern we must remember two things: the locations of the lines on the pattern at certain theta values as well as their relative intensity of the lines. So, these two together will constitute what is known as the diffraction pattern. So, no two elements or compounds or phases can have the same diffraction pattern.

So, any element compound or phase can be recognized by its corresponding diffraction pattern. So, this is a very important thing that we have found out that every material every element compound or phase will have its unique diffraction pattern characterized by the lines at some definite theta values and their relative intensities. So, this gives us a method of identifying an element or a compound or a phase.

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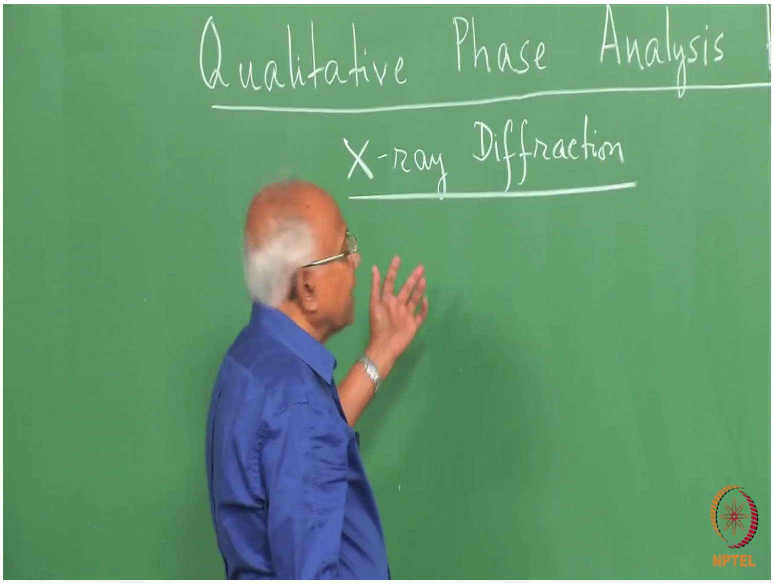

So, as we will see that this phase analysis you know can be done in a qualitative manner and also in a quantitative manner.

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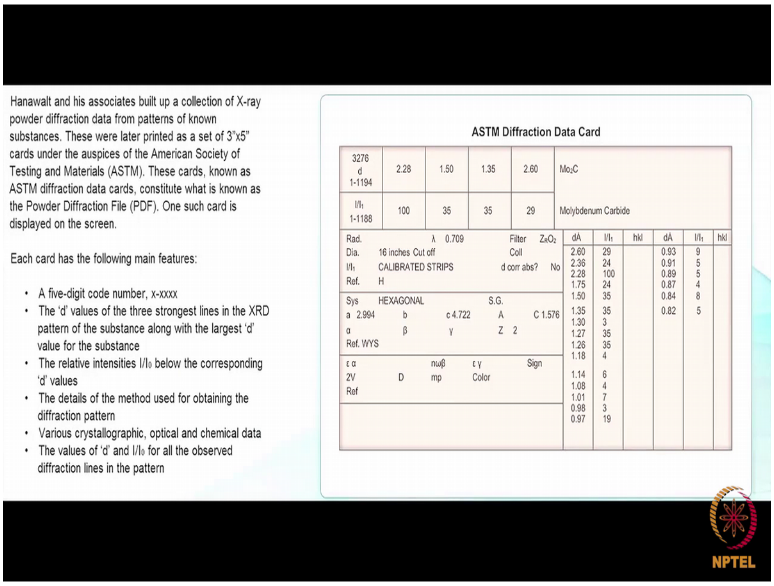

Hanawalt and his associates built up a collection of X-ray powder diffraction data from patterns of known substances. These were later printed as a set of 3"x5" cards under the auspices of the American Society of Testing and Materials (ASTM). These cards, known as ASTM diffraction data cards, constitute what is known as the Powder Diffraction File (PDF). One such card is displayed on the screen.

Each card has the following main features:

- A five-digit code number, x-xxxx
- The 'd' values of the three strongest lines in the XRD pattern of the substance along with the largest 'd' value for the substance
- The relative intensities I/I_0 below the corresponding 'd' values
- The details of the method used for obtaining the diffraction pattern
- Various crystallographic, optical and chemical data
- The values of 'd' and I/I_0 for all the observed diffraction lines in the pattern

ASTM Diffraction Data Card

3276 d 1-1194	2.28	1.50	1.35	2.60	Mo_2C
I/I_1 1-1188	100	35	35	29	Molybdenum Carbide

Rad. λ 0.709 Filter Z_RO_2
Dia. 16 inches Cut off Coll
I/I_1 CALIBRATED STRIPS d corr abs? No
Ref. H

Sys HEXAGONAL S.G.
a 2.994 b c 4.722 A C 1.576
α β γ Z 2
Ref. WYS

ε α nωβ ε γ Sign
2V D mp Color
Ref

dÅ	I/I_1	hkl	dÅ	I/I_1	hkl
2.60	29		0.93	9	
2.36	24		0.91	5	
2.28	100		0.89	5	
1.75	24		0.87	4	
1.50	35		0.84	8	
1.35	35		0.82	5	
1.30	3				
1.27	35				
1.26	35				
1.18	4				
1.14	6				
1.08	4				
1.01	7				
0.98	3				
0.97	19				

So, in this lecture, I will discuss about qualitative phase analysis by X-ray diffraction. Now this method evolved over a period of years and it owes a lot to the effort of Hanawalt.

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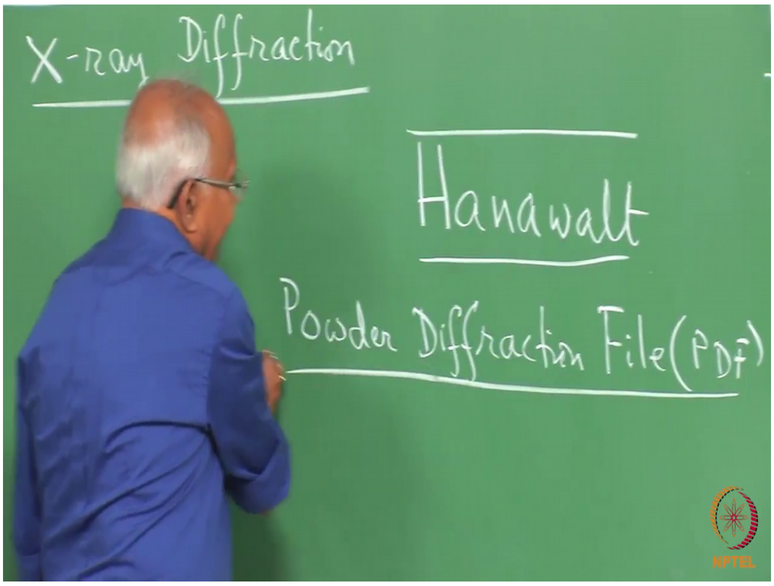

So, Hanawalt and his associates they built up a collection of X-ray powder diffraction data from patterns of known substances now these were later printed as a set of 3 inch by

5 inch cards under the auspices of the American society of testing materials now at ASTM diffraction data card is shown here these cards known as the ASTM diffraction data cards they constitute what is known as the powder diffraction file or PDF the powder diffraction file or PDF.

So, the powder diffraction file will consist of data from a large number of substances whose diffraction patterns were taken by researchers all over the world. Now if we look at a particular ASTM diffraction data card in the PDF, we will find the following characteristics following features there is a 5 digit number for each card then the d values of the 3 most strong lines in the XRD patterns of the substance along with their relative intensities are present say for example, in this case the 3 strongest lines have got d values of 2.28 angstrom 1.50 angstrom, 1.35 angstrom.

And the corresponding relative intensities are 135 and 35 in addition we also have the d value the highest d value that we can obtain from this material. So, this material shows the highest d value 2.6 which is recorded here and the corresponding relative intensity is also shown here now the method that has been used for obtaining the diffraction pattern of the material under consideration which is M o 2 c. In this particular case, those are shown over here this is followed by the various crystallographic optical and chemical data of this material here.

Now, finally, the values of d the interfere of distances and relative intensities I by I 0 for all the observed diffraction lines in the pattern are shown on the right hand side. So, along in this column the d values are recorded and here in this column the relative intensities same over here and here. So, this card represents a powder pattern completely. So, now, if we have say hundreds and thousands of materials whose X-ray diffraction patterns were taken by various researchers all over the world we can produce such a card for each different element compound or phase and put them for our future reference.

Now, what kind of what kind of method we can use for qualitatively determining the phase or you know the of an determine the identity of a unknown phase unknown elemental compound, we just take the diffraction pattern from the unknown material and try to compare the data for that particular material with the data provided in the many thousands of ASTM diffraction data cards and if we find that there is a match complete match of the diffraction pattern of the unknown material with that of the data in one of these cards then the identity of the unknown material becomes known. So, this is basically the method of qualitative phase analysis.

Now, you see when we have a large number of cards each card giving that diffraction data for one particular element or compound or phase then locating a card in the powder diffraction file may become quite time consuming and laborious.

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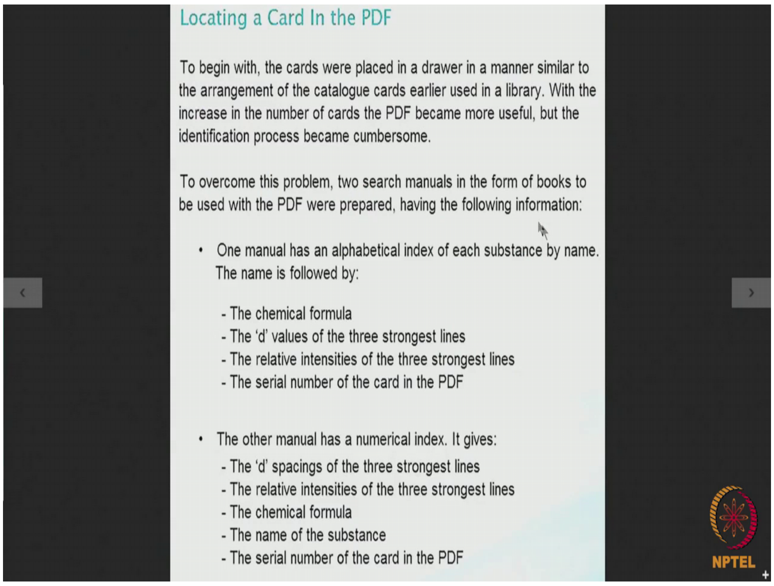

Locating a Card In the PDF

To begin with, the cards were placed in a drawer in a manner similar to the arrangement of the catalogue cards earlier used in a library. With the increase in the number of cards the PDF became more useful, but the identification process became cumbersome.

To overcome this problem, two search manuals in the form of books to be used with the PDF were prepared, having the following information:

- One manual has an alphabetical index of each substance by name. The name is followed by:
  - The chemical formula
  - The 'd' values of the three strongest lines
  - The relative intensities of the three strongest lines
  - The serial number of the card in the PDF
- The other manual has a numerical index. It gives:
  - The 'd' spacings of the three strongest lines
  - The relative intensities of the three strongest lines
  - The chemical formula
  - The name of the substance
  - The serial number of the card in the PDF

So, what is to be done to begin with these cards initially were placed in a dryer in a manner similar to the arrangement of the catalog cards earlier used in a library with the increase in the number of cards in the powder diffraction file the identification process became cumbersome to overcome this problem to search manuals in the form of books were prepared which are to be used with the powder diffraction file and these 2 books have the following information.

Now, one manual has an alphabetic index of each substance by name this name is followed by the chemical formula of the substance the d values of the 3 strongest lines the relative intensities of the 3 strongest lines and the serial number of the card in the powder diffraction file the other manual has a numerical index, it gives first that d spacings of the 3 strongest lines the relative intensities of the 3 strongest lines the chemical formula the name of the substance and the serial number of the card in the powder diffraction file. So, using these 2 manuals it becomes much easier to locate the desired card in the system of thousands of cards in the PDF.

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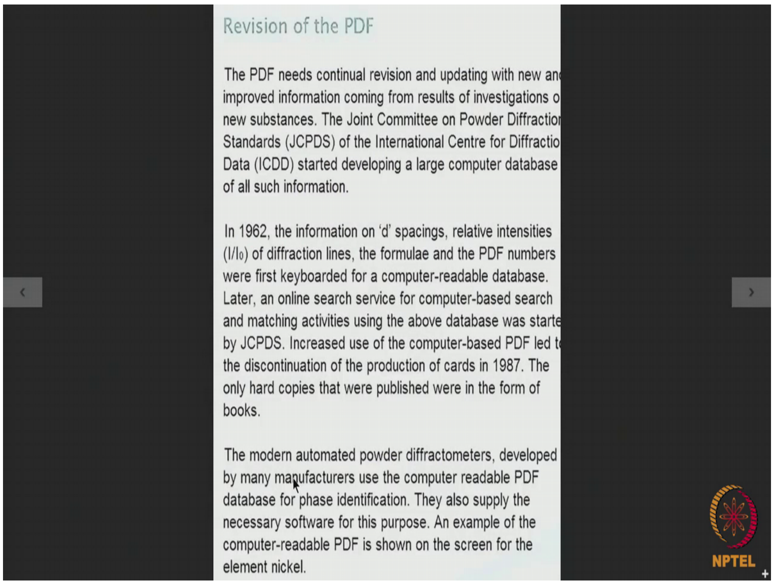

Revision of the PDF

The PDF needs continual revision and updating with new an improved information coming from results of investigations o new substances. The Joint Committee on Powder Diffractio Standards (JCPDS) of the International Centre for Diffractio Data (ICDD) started developing a large computer database of all such information.

In 1962, the information on 'd' spacings, relative intensities (I/I_0) of diffraction lines, the formulae and the PDF numbers were first keyboarded for a computer-readable database. Later, an online search service for computer-based search and matching activities using the above database was starte by JCPDS. Increased use of the computer-based PDF led t the discontinuation of the production of cards in 1987. The only hard copies that were published were in the form of books.

The modern automated powder diffractometers, developed by many manufacturers use the computer readable PDF database for phase identification. They also supply the necessary software for this purpose. An example of the computer-readable PDF is shown on the screen for the element nickel.

Now, the PDF is revised from time to time it needs continued revision and updating because new data on new substances become available from time to time. Now there has been a committee called the joint committee on powder diffraction standards in short JCPDS of the international center for diffraction data ICDD they started developing a large computer base of all such diffraction information from many many substances. So, in 1962 the information on d spacings relative intensities of diffraction lines the formulae and PDF numbers were first keyboarded for a computer readable database later an online search service for computer based search.

And matching activities using the above database was started by JCPDS increased use of the computer based PDF led to the discontinuation of the production of cards from nineteen eighty seven onwards the only hard copies that were published were in the form of books the modern automated powder diffractometers which was developed by many manufactures they use the computer readable powder diffraction file database for phase identification.

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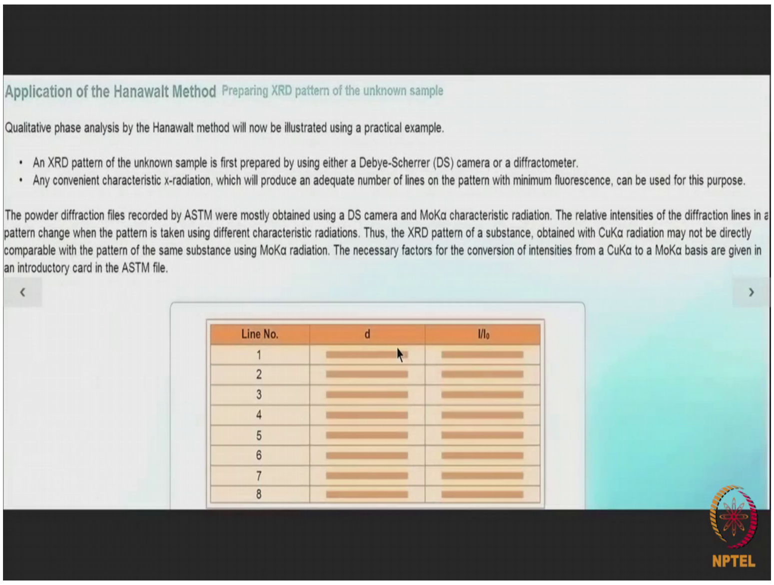

Application of the Hanawalt Method Preparing XRD pattern of the unknown sample

Qualitative phase analysis by the Hanawalt method will now be illustrated using a practical example.

- An XRD pattern of the unknown sample is first prepared by using either a Debye-Scherrer (DS) camera or a diffractometer.
- Any convenient characteristic x-radiation, which will produce an adequate number of lines on the pattern with minimum fluorescence, can be used for this purpose.

The powder diffraction files recorded by ASTM were mostly obtained using a DS camera and MoKα characteristic radiation. The relative intensities of the diffraction lines in a pattern change when the pattern is taken using different characteristic radiations. Thus, the XRD pattern of a substance, obtained with CuKα radiation may not be directly comparable with the pattern of the same substance using MoKα radiation. The necessary factors for the conversion of intensities from a CuKα to a MoKα basis are given in an introductory card in the ASTM file.

Line No.	d	I/I_0
1		
2		
3		
4		
5		
6		
7		
8		

They also supply the necessary software for this purpose. Now I will show the application of the Hanawalt method.

So, first we have to prepare the XRD pattern of the unknown sample either you can make it by the Debye Scherrer camera or using a diffractometer and we use a convenient x radiation a convenient characteristic X radiation which will produce an adequate number of lines on the pattern with minimum fluorescence; that means, minimum background radiation now the powder diffraction lines recorded in this manner were mostly using the molybdenum k alpha characteristic radiation. So, most of the diffraction patterns of many many substances were prepared by ASTM and they used a Debye Scherrer camera.

And a molybdenum k alpha characteristic radiation the relative intensities of the diffraction lines in a pattern may change when the pattern is taken using different characteristic radiations. So, this a very this is a very important fact to know thus the XRD pattern of a substance obtained it copper k alpha radiation may not be directly comparable with the pattern of the same substance using molybdenum k alpha radiation. So, the necessary factors for the conversion of intensities from copper k alpha to a molybdenum k alpha basis these are all given in an introduction card in the ASTM file.

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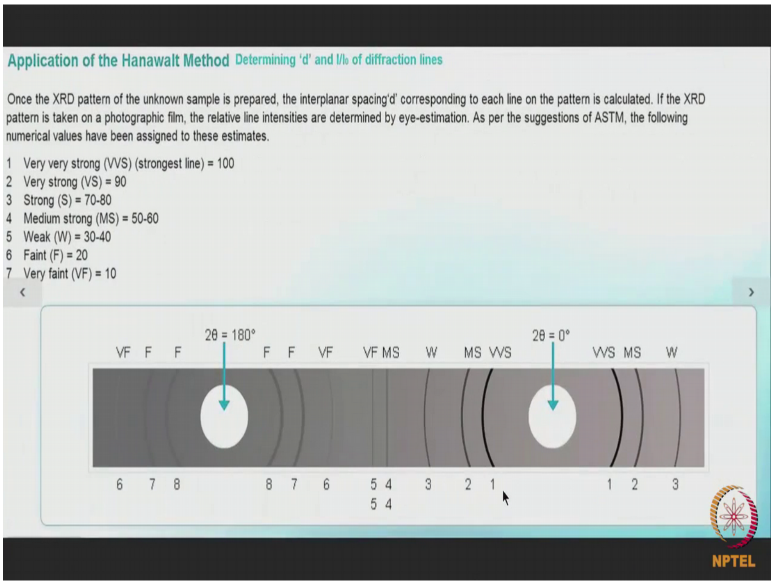

Application of the Hanawalt Method Determining 'd' and I/I₀ of diffraction lines

Once the XRD pattern of the unknown sample is prepared, the interplanar spacing'd' corresponding to each line on the pattern is calculated. If the XRD pattern is taken on a photographic film, the relative line intensities are determined by eye-estimation. As per the suggestions of ASTM, the following numerical values have been assigned to these estimates.

1 Very very strong (VVS) (strongest line) = 100
2 Very strong (VS) = 90
3 Strong (S) = 70-80
4 Medium strong (MS) = 50-60
5 Weak (W) = 30-40
6 Faint (F) = 20
7 Very faint (VF) = 10

So, this is a very important thing to remember now once a pattern is obtained the d values of all the lines present in the pattern are tabulated in this manner along with the relative intensity of each and every line say for example, we have got a powder pattern taken with a help of a Debye Scherrer camera as shown in the diagram now once the pattern is taken as I already said the interplanar spacings d is for each and every line pair are determined and what about the relative intensities normally the relative intensities are determined for the purpose of qualitative phase analysis by I estimation.

Again ASTM has suggested that the strongest line in the pattern should be given the tag very very strong VVS. So, its relative intensity is taken as 100 then comes the very strong or VS lines having relative intensity around ninety then comes the strong lines relative intensity it is 70 to 80 then comes the medium strong m s with relative intensity line between say 50 to 60 then comes the weak lines with relative intensities 30 to 40 the faint or F lines with relative intensity around 20 and very faint or VF lines with relative intensity of around 10. So, this type of a scale we normally use to estimate the relative intensities of the different lines in the pattern by I estimation as has been done in this particular case.

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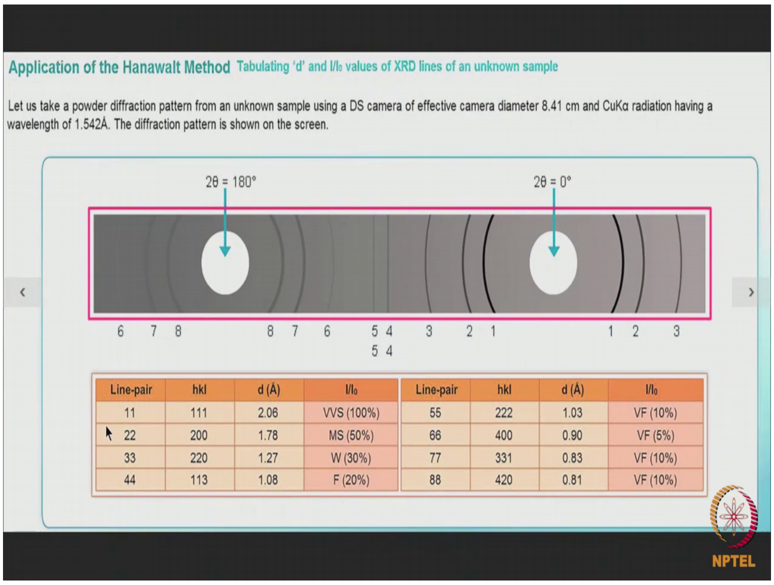

Application of the Hanawalt Method Tabulating 'd' and I/I₀ values of XRD lines of an unknown sample

Let us take a powder diffraction pattern from an unknown sample using a DS camera of effective camera diameter 8.41 cm and CuKα radiation having a wavelength of 1.542Å. The diffraction pattern is shown on the screen.

Line-pair	hkl	d (Å)	I/I_0	Line-pair	hkl	d (Å)	I/I_0
11	111	2.06	VVS (100%)	55	222	1.03	VF (10%)
22	200	1.78	MS (50%)	66	400	0.90	VF (5%)
33	220	1.27	W (30%)	77	331	0.83	VF (10%)
44	113	1.08	F (20%)	88	420	0.81	VF (10%)

Now, say for example, we have taken the Debye Scherrer diffraction pattern from an unknown sample having an effective camera radius or camera diameter of say 8.41 centimeter and copper k alpha radiation having a wavelength of 1.542 angstrom the diffraction pattern is shown on the screen and from each and every line pair, we could find out their HKL values in the usual manner and their DS together with the relative intensities now once we do that; we have to compare this data for the unknown substance with the diffraction data that is from many many substances many thousands of substances that are available in the powder diffraction file.

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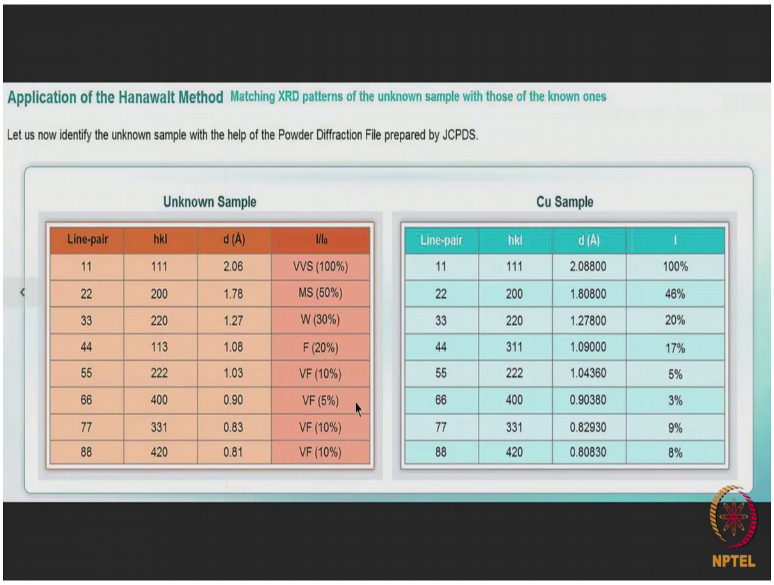

Application of the Hanawalt Method Matching XRD patterns of the unknown sample with those of the known ones

Let us now identify the unknown sample with the help of the Powder Diffraction File prepared by JCPDS.

Unknown Sample

Line-pair	hkl	d (Å)	I/I_0
11	111	2.06	VVS (100%)
22	200	1.78	MS (50%)
33	220	1.27	W (30%)
44	113	1.08	F (20%)
55	222	1.03	VF (10%)
66	400	0.90	VF (5%)
77	331	0.83	VF (10%)
88	420	0.81	VF (10%)

Cu Sample

Line-pair	hkl	d (Å)	I
11	111	2.08800	100%
22	200	1.80800	46%
33	220	1.27800	20%
44	311	1.09000	17%
55	222	1.04360	5%
66	400	0.90380	3%
77	331	0.82930	9%
88	420	0.80830	8%

So, now how we identify that we look into the PDF and figure out with which card with which data; the data in which card in the PDF matches pretty well with the data that have been obtained from the unknown material. Say for example, our unknown sample; this shows all these 8 lines they are HKL values they are d values and their relative intensities and once we start matching these data with the data provided in the thousands of cards that are available in the PDF we find that these data match pretty well with the data provided for anode copper sample.

So, as you can see here the HKLs all match that DS you know they match to a very great extent and the relative intensities also match to a very great extent that shows the unknown sample must be pure copper now in this way, whenever we have the X-ray diffraction data has been taken from an unknown sample then simply by comparing the data in the XRD pattern of the unknown if we compare it with the data provided in the; for the many thousands of substances which are available in the powder diffraction file it becomes quite easy to figure out what the unknown sample could be.