INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
NPTEL
NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
Lecture- 16
Qualitative Analysis by Diffraction
With
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Hello, in this particular lecture actually we were going to discuss about the qualitative analysis by diffraction. So that means, if we are having any samples maybe, we don’t know the crystal structure or maybe the elemental information’s of that particular materials. So how we are going to know that which type of material it is? Or maybe what is the chemical formula of that particular material?

So qualitative analysis what does it mean actually? So qualitative analysis is the identifications of the constituents as I told already that means elements or maybe the functional groups present in a substance.

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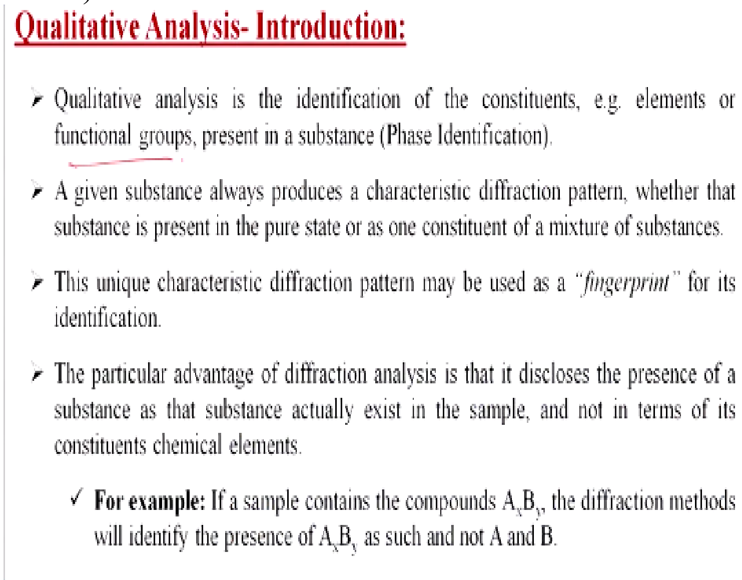

Qualitative Analysis- Introduction:

- Qualitative analysis is the identification of the constituents, e.g. elements or functional groups, present in a substance (Phase Identification).
- A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances.
- This unique characteristic diffraction pattern may be used as a *"fingerprint"* for its identification.
- The particular advantage of diffraction analysis is that it discloses the presence of a substance as that substance actually exist in the sample, and not in terms of its constituents chemical elements.
  - ✓ **For example:** If a sample contains the compounds A_xB_y, the diffraction methods will identify the presence of A_xB_y as such and not A and B.

That means face identifications a given substance always produce a characteristic diffraction pattern, whether that substance is present in the pure state or as one of the constituent of a mixture of substances say suppose copper, if it is in the pure form of copper or maybe some cuprous oxide C2O or maybe something other else. The unique characteristic diffraction pattern maybe used as a fingerprint for its identification, so simple it will give you the whole information.

The particular advantage of diffraction analysis is that, it discloses the presence of a substance as that substance actually exist in the sample, and not in terms of its constituents chemical elements. Say suppose, for example if a sample contains the compounds AX, BY the diffractions methods will identify the presence of AX, BY as such and not A and B.

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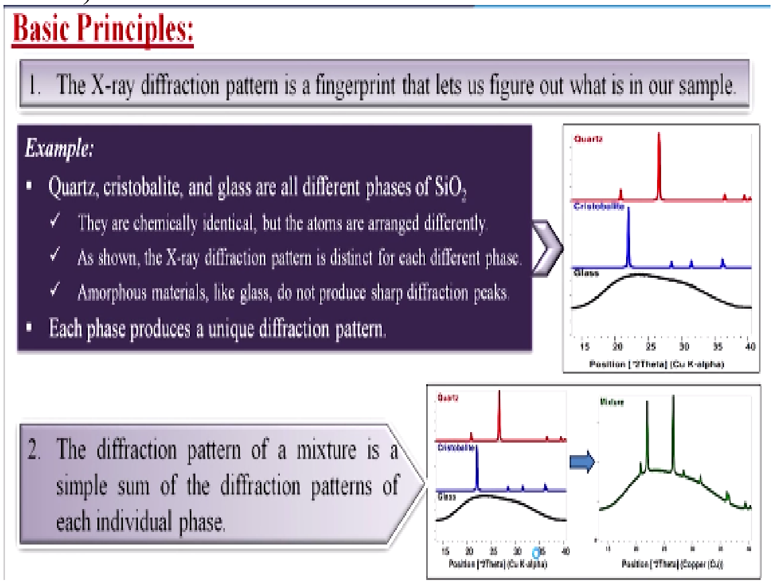

Basic Principles:

1. The X-ray diffraction pattern is a fingerprint that lets us figure out what is in our sample.

Example:

- Quartz, cristobalite, and glass are all different phases of SiO_2
  - ✓ They are chemically identical, but the atoms are arranged differently.
  - ✓ As shown, the X-ray diffraction pattern is distinct for each different phase.
  - ✓ Amorphous materials, like glass, do not produce sharp diffraction peaks.
- Each phase produces a unique diffraction pattern.

2. The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.

So how actually it is doing? I mean so what is the basic principles? The x-ray diffraction pattern is a fingerprint that later figure out what is in our sample? For example, say suppose quartz cristobalite and glass are all different faces of the silicon dioxide. They are chemically identical but the atoms are arranged differently. As shown, the x-ray diffraction pattern is distinct for each different face, so for glass there is no sharp peaks it is very much broaden.

For cristobalite it is showing some sharp peaks around 22° and for quartz it is showing some sharp peak around maybe 27°. Amorphous materials like glass do not produce the sharp diffraction peaks. Each face produces a unique diffraction pattern form this image we have seen. The diffraction pattern of a mixture is a simple sum of the diffraction pattern of each individual face, so suppose I am having one material in which this three faces are present.

So I will get the image like this, so this is for the quartz you can see a small peaks are coming like this one and then it is having some broad peak which is for the glass and then it is showing the cristobalite preachy at this particular point. So that will be a combination of all the peaks.

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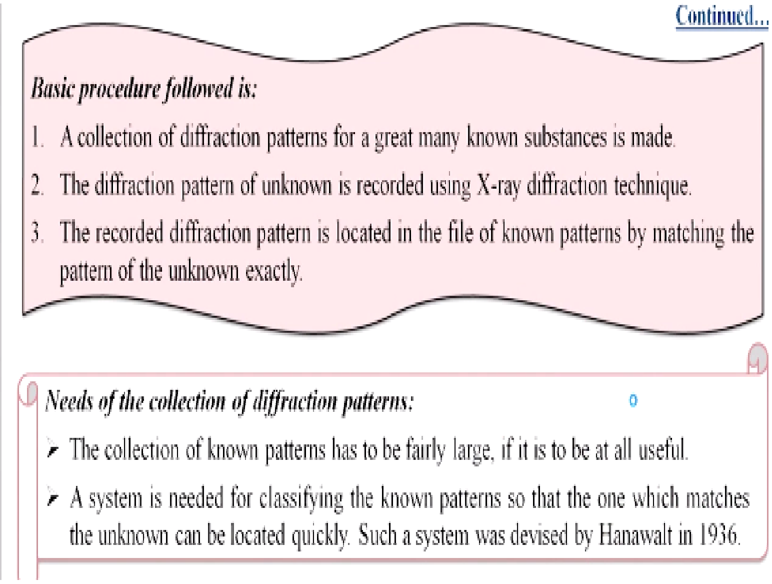

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Basic procedure followed is:

1. A collection of diffraction patterns for a great many known substances is made.
2. The diffraction pattern of unknown is recorded using X-ray diffraction technique.
3. The recorded diffraction pattern is located in the file of known patterns by matching the pattern of the unknown exactly.

Needs of the collection of diffraction patterns:

- The collection of known patterns has to be fairly large, if it is to be at all useful.
- A system is needed for classifying the known patterns so that the one which matches the unknown can be located quickly. Such a system was devised by Hanawalt in 1936.

Basic procedure generally which we are following is that a collection of diffraction patterns for a great many known substance is already made. The diffraction pattern of unknown is recorded using x-ray diffraction technique. The recorded diffraction pattern is located in the file of known patterns by matching the patterns of the unknown exactly. So why we need the collection of diffraction patterns, the collection of known patterns has to be fairly large if it is to be at all useful.

A system is needed for classifying the known patterns so that the one which matches the unknown can be located quickly. Such a system was devised by Hanawalt in 1936. Actually simple we are having one database of all the known samples so maximum times we are matching our samples with that database whether this is the same sample or not and if something new then only we are trying to finds out what are the new samples? So if I go through the history first in the year of 1936.

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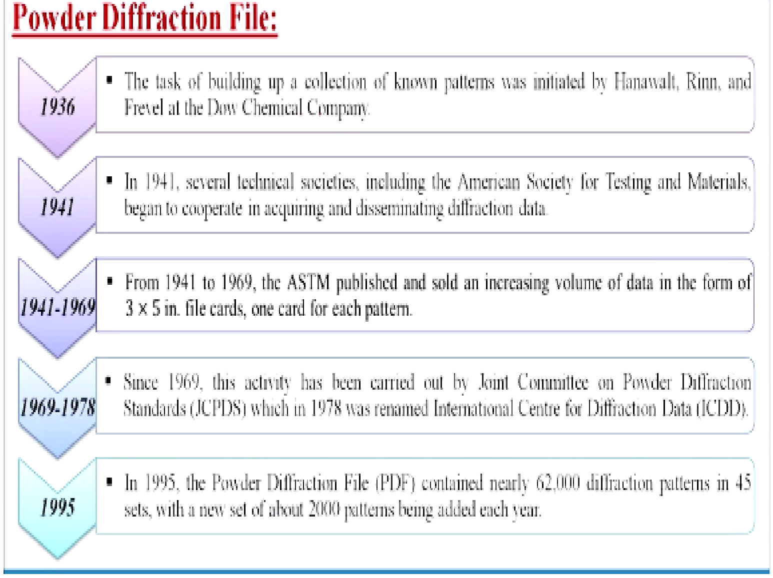

Powder Diffraction File:

1936
- The task of building up a collection of known patterns was initiated by Hanawalt, Rinn, and Frevel at the Dow Chemical Company.

1941
- In 1941, several technical societies, including the American Society for Testing and Materials, began to cooperate in acquiring and disseminating diffraction data.

1941-1969
- From 1941 to 1969, the ASTM published and sold an increasing volume of data in the form of 3 x 5 in. file cards, one card for each pattern.

1969-1978
- Since 1969, this activity has been carried out by Joint Committee on Powder Diffraction Standards (JCPDS) which in 1978 was renamed International Centre for Diffraction Data (ICDD).

1995
- In 1995, the Powder Diffraction File (PDF) contained nearly 62,000 diffraction patterns in 45 sets, with a new set of about 2000 patterns being added each year.

The task of building up a collection of known pattern was initiated by Hanawalt, Rinn and frevel at the Dow chemical company. In 1941, several technical's society including the American society for testing and materials that is AHTM began to co-operate in acquiring an, disseminating diffraction data. In the year from 1941 to 1969 the ASTM published and sold an increasing volume of data in the form of three into five inch file cards, one card for each pattern.

So they are having a number of cards, in number of cards each and every sample diffraction patterns has been given with full information's. From 1969 to 1978 this activity has been carried out by joint committee on powder diffraction standards which is called the JCPDS, so that is why we are calling it as a JCPDS file which in 1978 was renamed international centre for diffraction data or maybe the ICDD.

In 1995 the powder diffraction file PDF contained nearly 62,000 diffraction patterns in 45 sets. With a new set of about 2000 patterns being added each year, because from a material scientist point of view, in a lab every day all the scientist or maybe the students, they are preparing the new, new materials. So the new, new crystal structures are forming so automatically that data base is going to be upgraded every year.

Now first, let us know what is Hanawalt method? So a powder pattern is characterized by a set of line positions.

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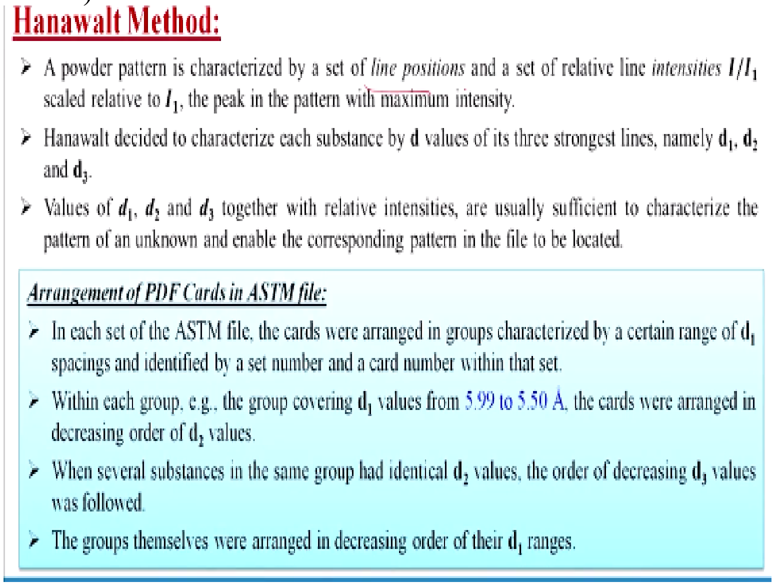

Hanawalt Method:

- A powder pattern is characterized by a set of *line positions* and a set of relative line *intensities* I/I_1 scaled relative to I_1, the peak in the pattern with maximum intensity.
- Hanawalt decided to characterize each substance by **d** values of its three strongest lines, namely d_1, d_2 and d_3.
- Values of d_1, d_2 and d_3 together with relative intensities, are usually sufficient to characterize the pattern of an unknown and enable the corresponding pattern in the file to be located.

Arrangement of PDF Cards in ASTM file:

- In each set of the ASTM file, the cards were arranged in groups characterized by a certain range of d_1 spacings and identified by a set number and a card number within that set.
- Within each group, e.g., the group covering d_1 values from 5.99 to 5.50 Å, the cards were arranged in decreasing order of d_2 values.
- When several substances in the same group had identical d_2 values, the order of decreasing d_3 values was followed.
- The groups themselves were arranged in decreasing order of their d_1 ranges.

And a set of relative line intensities that is I/I1 scaled relative to I1 the peak in the pattern with maximum intensity. So Hanawalt decided to characterize each substance buy devalue of its three strongest lines namely, D1, D2 and D3. So I is the biggest intensity and I1, I2, I3 are the individual intensity of different peaks. So values of D1, D2 and D3 together with relative intensities are usually sufficient to characterize the pattern of an unknown and enable the corresponding pattern in the file to be located.

What is the arrangement of PDF cards in ASTM file? In each set of the ASTM file the cards were arranged in groups characterized by a certain range of D1 spacing's and identified by a set of number and a card number within that set. Within each group for example the group covering

D1 values from 5.99 to 5.50 which I am going to show you the example in the next slide. The cards were arranged in decreasing order of D2 values.

When several substances in the same group had identical D2 values the order of decreasing D3 values was followed, so D1 is ranging from 5.99 to 5.50. Within that D1 range what is the D2 value? Just we are arranging in the decreasing order, then when D2 has completed and D3 also in the decreasing order. So the groups themselves were arranged in decreasing order of their D1 ranges so how to do that one?

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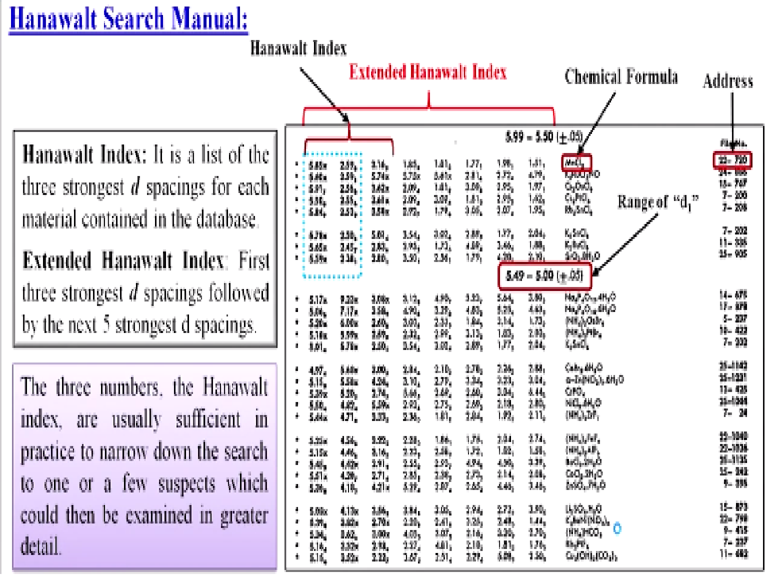

Hanawalt Search Manual:

Hanawalt Index: It is a list of the three strongest *d* spacings for each material contained in the database.

Extended Hanawalt Index: First three strongest *d* spacings followed by the next 5 strongest d spacings.

The three numbers, the Hanawalt index, are usually sufficient in practice to narrow down the search to one or a few suspects which could then be examined in greater detail.

So Hanawalt index, it is a least of three strongest D spacing's for each material contained in the database D1, D2, D3 and there are soon. Like D4, D5, D6 BUT d1, d2, d3 we are assuming these are the strongest one. Extended Hanawalt index first three strongest D spaces followed by the next five strongest D spacing so this is the, extended one. The three numbers the Hanawalt index are usually sufficient in practice to narrow down the search to one or a few suspects which could then be examined in greater details.

So simple you can see that D2 value just we are going into the decreasing order which is ranging from 5.99 to 5.50 D1 value. So like this way then after that we will go for the D3 and here we will get the fine number over there.

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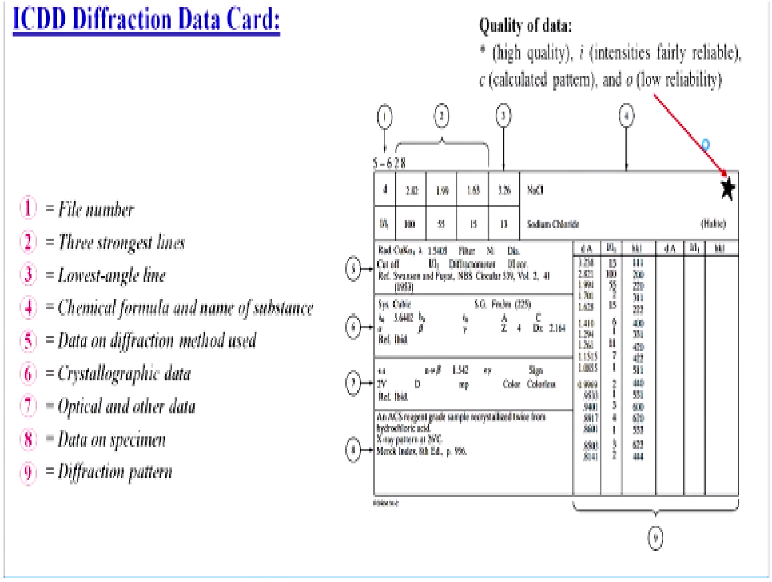

ICDD Diffraction Data Card:

Quality of data:
* (high quality), *i* (intensities fairly reliable), *c* (calculated pattern), and *o* (low reliability)

① = *File number*
② = *Three strongest lines*
③ = *Lowest-angle line*
④ = *Chemical formula and name of substance*
⑤ = *Data on diffraction method used*
⑥ = *Crystallographic data*
⑦ = *Optical and other data*
⑧ = *Data on specimen*
⑨ = *Diffraction pattern*

So now if we see the ICDD diffraction data card it looks like this, which one means this one is, give you the file number to this the D1, D2 and D3 three strongest line over there the lowest angle lines over there is the three. Four chemical formulas and the name of the substance, in this case it is sodium chloride chemical formula and then star has been given, star means it is high quality.

If it is been written I that means intensities fairly reliable, if C will written over there then C is the calculated pattern and O means it is low reliability. Next five is the data on diffraction method used, so five here what is the data? What is the copper key λ value? And what is the data on the diffraction methods means input parameters? Six is the crystallographic data over there so it will give you the λ, β, γ all the values over there. seven optical and other data given over there, eight is the data on specimen, so this is the data on specimen and nine will be the diffraction pattern over there that H K L value it will give you.

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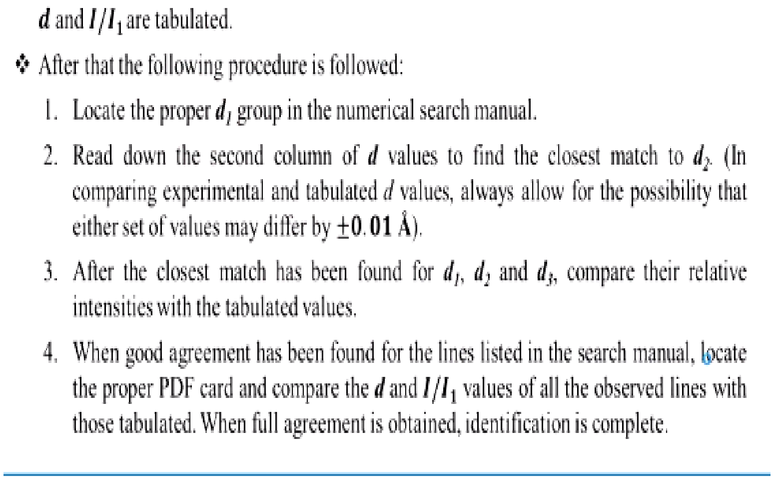

Procedure for Identifying Unknown Samples:

- ❖ The diffraction pattern of the unknown sample is recorded and the experimental values of d and I/I_1 are tabulated.
- ❖ After that the following procedure is followed:
  1. Locate the proper d_1 group in the numerical search manual.
  2. Read down the second column of d values to find the closest match to d_2. (In comparing experimental and tabulated d values, always allow for the possibility that either set of values may differ by ± 0.01 Å).
  3. After the closest match has been found for d_1, d_2 and d_3, compare their relative intensities with the tabulated values.
  4. When good agreement has been found for the lines listed in the search manual, locate the proper PDF card and compare the d and I/I_1 values of all the observed lines with those tabulated. When full agreement is obtained, identification is complete.

So now procedure for identifying the unknown samples, so the diffraction pattern of the unknown sample is recorded and the experimental values of D and I/I1 are tabulated. After that the following procedure is followed, first locate the proper D1 group in the numerical search manual. Read down the second column of D values to find the closest match to D2 in comparing the experimental and tabulated D values always allow for the possibility that either set of values may differ by + - 0.01 Angstrom.

After the closest match has been found for D1, D2 and D3 compare the relative intensities with that tabulated values. When good agreement has been found for the lines listed in the search manual look at the proper PDF card and compare the D and I/I1 values of all the observed lines with those tabulated. When full agreement is obtained, identification is complete.

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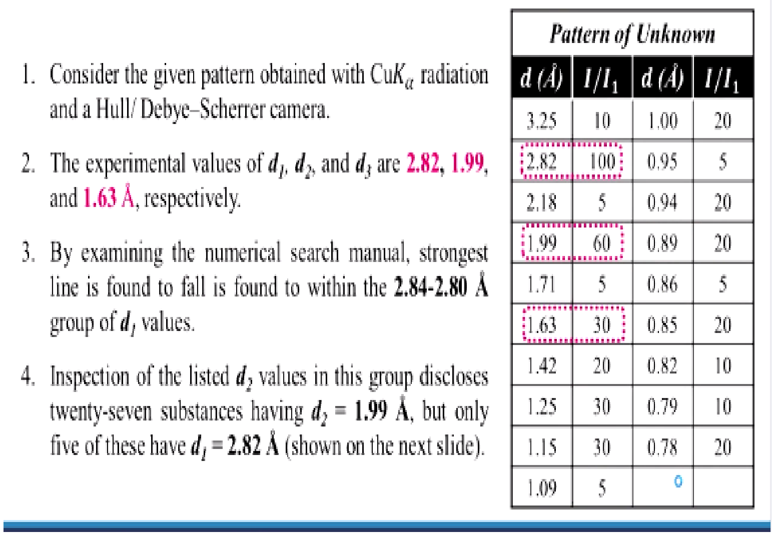

Identification of Single Phase Samples- (*Example*):

1. Consider the given pattern obtained with CuK_α radiation and a Hull/ Debye–Scherrer camera.
2. The experimental values of d_1, d_2, and d_3 are 2.82, 1.99, and 1.63 Å, respectively.
3. By examining the numerical search manual, strongest line is found to fall is found to within the **2.84-2.80 Å** group of d_1 values.
4. Inspection of the listed d_2 values in this group discloses twenty-seven substances having d_2 = **1.99 Å**, but only five of these have d_1 = **2.82 Å** (shown on the next slide).

Pattern of Unknown

d (Å)	I/I_1	d (Å)	I/I_1
3.25	10	1.00	20
2.82	100	0.95	5
2.18	5	0.94	20
1.99	60	0.89	20
1.71	5	0.86	5
1.63	30	0.85	20
1.42	20	0.82	10
1.25	30	0.79	10
1.15	30	0.78	20
1.09	5		

so identification of a single phase samples, so it is an example so first consider the given pattern obtain for copper K λ radiations all the hull Debye-Scherrer camera, the experimental values of d1, d2, and d3 are 2.82, 1.99 and 1.63. Because in this case the I/I1 is the maximum so that is why it is d1 and then the second one is sixty so that is why 1.99 is d2 and next one is the 30 that is 1.63 is any rest of the d4, d5, and d6 like that.

By examining the numerical search manual strongest line is found to within the 2.84 to 2.80 Angstrom group of d1 values. Inspection of the listed d2 values in this group discloses twenty seven substances having d2 is equal to 1.99 Angstrom but only five of these have d1 is equal to 2.82 Angstrom shown on the next slide.

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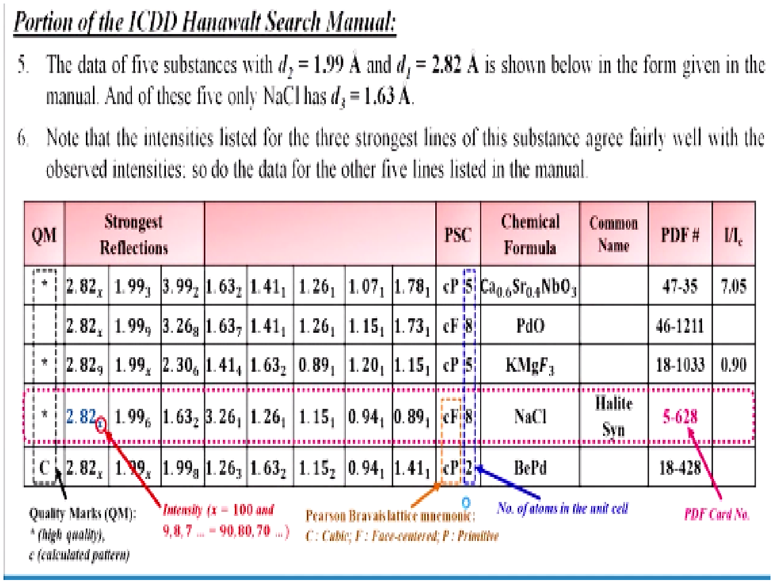

Portion of the ICDD Hanawalt Search Manual:

5. The data of five substances with d_2 = 1.99 Å and d_1 = 2.82 Å is shown below in the form given in the manual. And of these five only NaCl has d_3 = 1.63 Å.
6. Note that the intensities listed for the three strongest lines of this substance agree fairly well with the observed intensities: so do the data for the other five lines listed in the manual.

QM	Strongest Reflections								PSC		Chemical Formula	Common Name	PDF #	I/I_c
*	2.82_x	1.99_3	3.99_2	1.63_2	1.41_1	1.26_1	1.07_1	1.78_1	cP	5	$Ca_{0.6}Sr_{0.4}NbO_3$		47-35	7.05
	2.82_x	1.99_9	3.26_8	1.63_7	1.41_1	1.26_1	1.15_1	1.73_1	cF	8	PdO		46-1211	
*	2.82_9	1.99_x	2.30_6	1.41_4	1.63_2	0.89_1	1.20_1	1.15_1	cP	5	$KMgF_3$		18-1033	0.90
*	2.82_x	1.99_6	1.63_2	3.26_1	1.26_1	1.15_1	0.94_1	0.89_1	cF	8	NaCl	Halite Syn	5-628	
C	2.82_x	1.99_x	1.99_8	1.26_3	1.63_2	1.15_2	0.94_1	1.41_1	cP	2	BePd		18-428	

Quality Marks (QM):
* (high quality),
c (calculated pattern)

Intensity (x = 100 and 9, 8, 7 ... = 90, 80, 70 ...)

Pearson Bravais lattice mnemonic:
C : Cubic; F : Face-centered; P : Primitive

No. of atoms in the unit cell

PDF Card No.

So in this particular case you can find that 2.82 and d2 is matching 1.99 over there. so now five is the data five substances with d2 is equal to 1.99 Angstrom and d1 is equal to 2.82 Angstrom is shown below in the form given in the manual and of this five only MACL has d3. So first we have matched d1, then we are matching the d2 and then we are matching the d3. Note that the intensity is listed for three strongest lines of this substance agree fairly well with the observed intensities, so do the data for the other five lines listed in the manual.

So when d1, d2, d3 matching has been completed then we will go for the rest one, so from these we can get that it is C, C means already I told you that is calculated patterns if it is some kind of mark astorics so it is high quality, then X is the intensity say suppose 100%, 30%, 40%, 60% like that. Then CP C is the cubic F is the face centered and P is the primitive, here two means number of atoms in the unit and this is the PDF card number that is 5-628.

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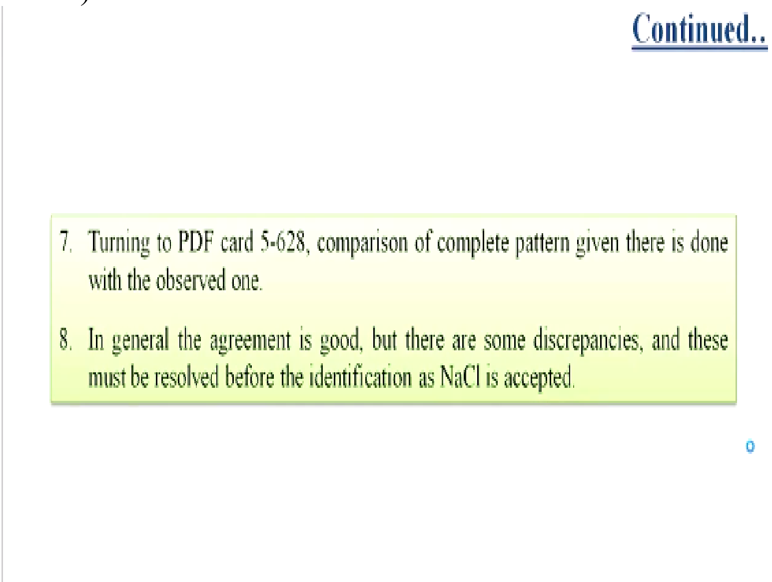

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7. Turning to PDF card 5-628, comparison of complete pattern given there is done with the observed one.
8. In general the agreement is good, but there are some discrepancies, and these must be resolved before the identification as NaCl is accepted.

So now turning to PDF card 5-628 comparison of complete pattern given there is done with the observed one. In general the agreement is good but there are some discrepancies and this must be resolved before the identification as sodium chloride is accepted.

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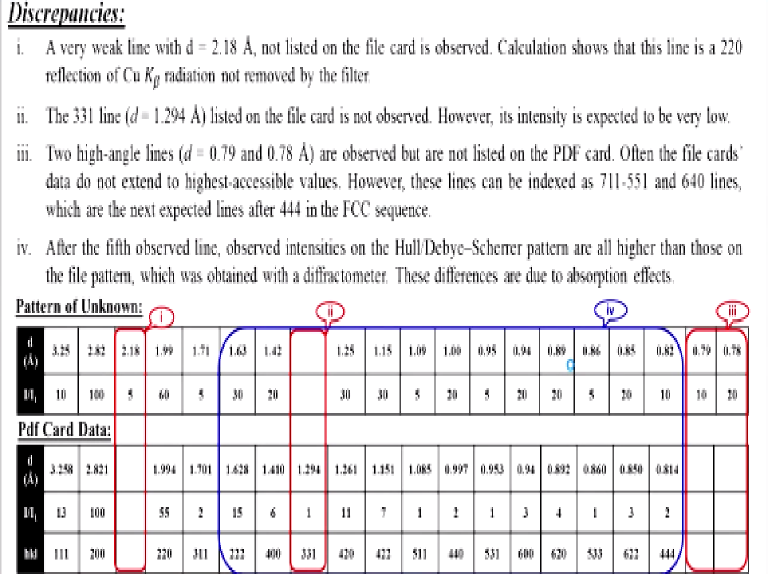

Discrepancies:

i. A very weak line with d = 2.18 Å, not listed on the file card is observed. Calculation shows that this line is a 220 reflection of Cu K_β radiation not removed by the filter.

ii. The 331 line (d = 1.294 Å) listed on the file card is not observed. However, its intensity is expected to be very low.

iii. Two high-angle lines (d = 0.79 and 0.78 Å) are observed but are not listed on the PDF card. Often the file cards' data do not extend to highest-accessible values. However, these lines can be indexed as 711-551 and 640 lines, which are the next expected lines after 444 in the FCC sequence.

iv. After the fifth observed line, observed intensities on the Hull/Debye–Scherrer pattern are all higher than those on the file pattern, which was obtained with a diffractometer. These differences are due to absorption effects.

Pattern of Unknown:

d (Å)	3.25	2.82	2.18	1.99	1.71	1.63	1.42		1.25	1.15	1.09	1.00	0.95	0.94	0.89	0.86	0.85	0.82	0.79	0.78
I/I_1	10	100	5	60	5	30	20		30	30	5	20	5	20	20	5	20	10	10	20

Pdf Card Data:

d (Å)	3.258	2.821		1.994	1.701	1.628	1.410	1.294	1.261	1.151	1.085	0.997	0.953	0.94	0.892	0.860	0.850	0.814		
I/I_1	13	100		55	2	15	6	1	11	7	1	2	1	3	4	1	3	2		
hkl	111	200		220	311	222	400	331	420	422	511	440	531	600	620	533	622	444		

What are the discrepancies? A very week line with d is equal to 2.18 Angstrom not listed on the file card is observed, calculations of this one. Calculations show that this line is a 220 reflection of copper K β radiations not removed by the filter itself. The 331 line which is nothing but d is equal to 1.294 Angstrom so listed on the file card is not observed over there, so in this particular case however it is intensity is expected to be very low.

Two high angles that is d is equal to 0.79 and .78 Angstrom are all observed but are not listed on the PDF card, often the file cards data do not extend to highest accessible values. However this line can be indexed as 711-551 and 640 lines which are the next expected lines after 444 in the FCC sequence. After the fifth observed lines observed intensities on the hull Debye-Scherrer pattern are all higher than those on the file pattern.

Which was obtained with diffractometer, this differences are due to absorption effects over there.

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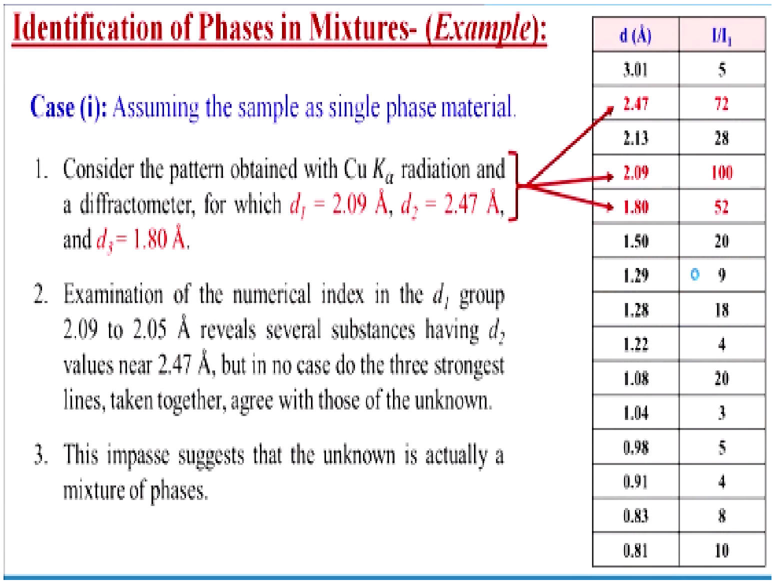

Identification of Phases in Mixtures- (*Example*):

Case (i): Assuming the sample as single phase material.

1. Consider the pattern obtained with Cu K_α radiation and a diffractometer, for which $d_1 = 2.09$ Å, $d_2 = 2.47$ Å, and $d_3 = 1.80$ Å.
2. Examination of the numerical index in the d_1 group 2.09 to 2.05 Å reveals several substances having d_2 values near 2.47 Å, but in no case do the three strongest lines, taken together, agree with those of the unknown.
3. This impasse suggests that the unknown is actually a mixture of phases.

d (Å)	I/I_1
3.01	5
2.47	72
2.13	28
2.09	100
1.80	52
1.50	20
1.29	9
1.28	18
1.22	4
1.08	20
1.04	3
0.98	5
0.91	4
0.83	8
0.81	10

Now identification of faces in mixtures, say suppose I am having a combinations of materials so how to do that? First case 1 assuming the samples as single phase material, so first consider the pattern obtained with copper K λ radiations and diffractometer for which d1 is equal to 2.09 here then will be d2 2.47 and d3 will be 1.80 Angstrom. Examination of the numerical index in the d1 group 2.90 to 2.05 Angstrom reveals several substances having d2 value near 2.47 Angstrom.
But in no case to the three strongest lines taken together agree with those of the unknown. This impasse suggests that the unknown is actually a mixture of phases.
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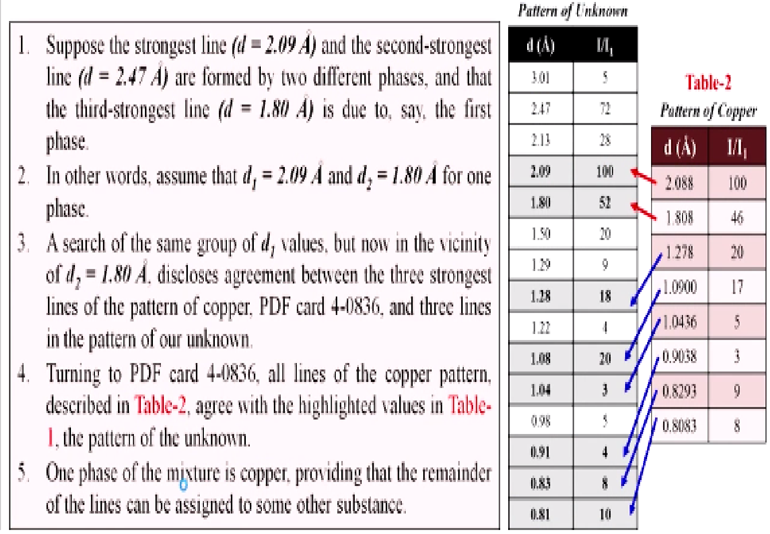

Case (ii): Assuming the sample as mixture of two phases.

1. Suppose the strongest line (*d = 2.09 Å*) and the second-strongest line (*d = 2.47 Å*) are formed by two different phases, and that the third-strongest line (*d = 1.80 Å*) is due to, say, the first phase.
2. In other words, assume that $d_1 = 2.09$ Å and $d_2 = 1.80$ Å for one phase.
3. A search of the same group of d_1 values, but now in the vicinity of $d_2 = 1.80$ Å, discloses agreement between the three strongest lines of the pattern of copper, PDF card 4-0836, and three lines in the pattern of our unknown.
4. Turning to PDF card 4-0836, all lines of the copper pattern, described in Table-2, agree with the highlighted values in Table-1, the pattern of the unknown.
5. One phase of the mixture is copper, providing that the remainder of the lines can be assigned to some other substance.

Table-1

Pattern of Unknown

d (Å)	I/I_1
3.01	5
2.47	72
2.13	28
2.09	100
1.80	52
1.50	20
1.29	9
1.28	18
1.22	4
1.08	20
1.04	3
0.98	5
0.91	4
0.83	8
0.81	10

Table-2

Pattern of Copper

d (Å)	I/I_1
2.088	100
1.808	46
1.278	20
1.0900	17
1.0436	5
0.9038	3
0.8293	9
0.8083	8

Case 2, assuming the sample as mixture of two faces, so in this case what we are going to do. Suppose the strongest line d is equal to 2.09 and the second strongest line d is equal to 2.47 and are formed by two different phases and that the third strongest line d is equal to 1.80 is due to say the first phase. In other word assume that d1 is equal to 2.09 Angstrom and d2 is equal to 1.80 Angstrom for one phase is search of the same group of d1 values, but now in the vicinity of d2

1.80 Angstrom discloses agreement between the three strongest lines of the pattern of copper. PDF card 4-0836 and three lines in the pattern of our unknown.

So in this case actually what happen two peaks are matching properly, this two peaks and this is one matching. So first we have identified the copper and then again we will go for the unknown peak and then through that unknown peak also we will get the d1, d2, and d3 value and then on that peak, again I am going to match you with the JCPDS file or maybe with the PDF card. Turning to PDF card 4-0836 all line of the copper pattern described in table 2, agree with the highlighted value in table 1, the pattern of the unknown itself.

So this two are matching properly and rest of the lines we are going to match means this two are matching, this 1,2, 3, 4, 5, 6 and 7 seven these seven peaks are not matching and these rest of the peaks also are matching with these table two. One face of the mixture is copper providing that the reminder of the lines can be assigned to some other substance.

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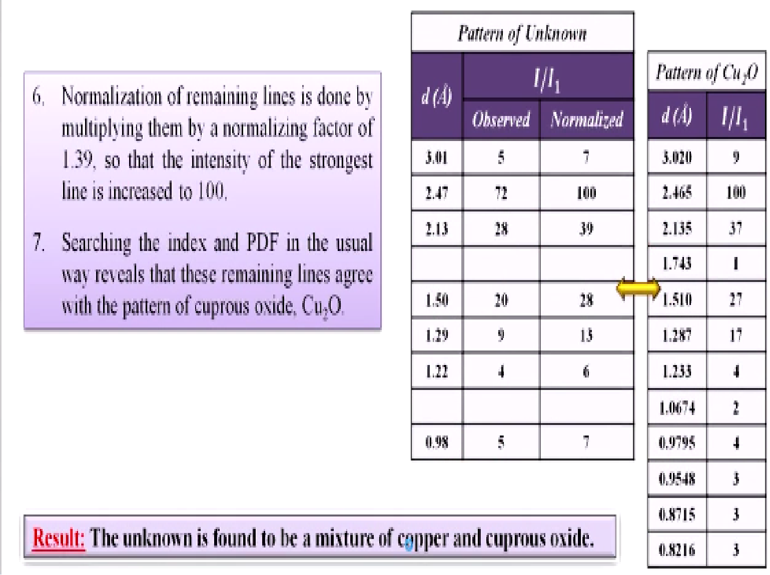

6. Normalization of remaining lines is done by multiplying them by a normalizing factor of 1.39, so that the intensity of the strongest line is increased to 100.
7. Searching the index and PDF in the usual way reveals that these remaining lines agree with the pattern of cuprous oxide, Cu_2O.

Pattern of Unknown

d (Å)	I/I_1	
	Observed	Normalized
3.01	5	7
2.47	72	100
2.13	28	39
1.50	20	28
1.29	9	13
1.22	4	6
0.98	5	7

Pattern of Cu_2O

d (Å)	I/I_1
3.020	9
2.465	100
2.135	37
1.743	1
1.510	27
1.287	17
1.233	4
1.0674	2
0.9795	4
0.9548	3
0.8715	3
0.8216	3

Result: The unknown is found to be a mixture of copper and cuprous oxide.

How normalization of remaining lines is done by multiplying them by a normalizing factor of 1.39, so that the intensity of the strongest line is increased to hundred, so you can see that observed we have got the 72 intensity, now we are taking 72 as a 100 and then we are doing the normalizing one. So in this particular case 2.47 will become the d1 value, and then the next one will become 2.13 and 1.50.

Now we are going to match with some other card so this is matching with Cu2O. Searching the index and PDF in the usual way reveals that these remaining lines agree with the pattern of cuprous oxide which is nothing but the Cu2O. Result, the unknown is found to be a mixture of copper and the cuprous oxide.

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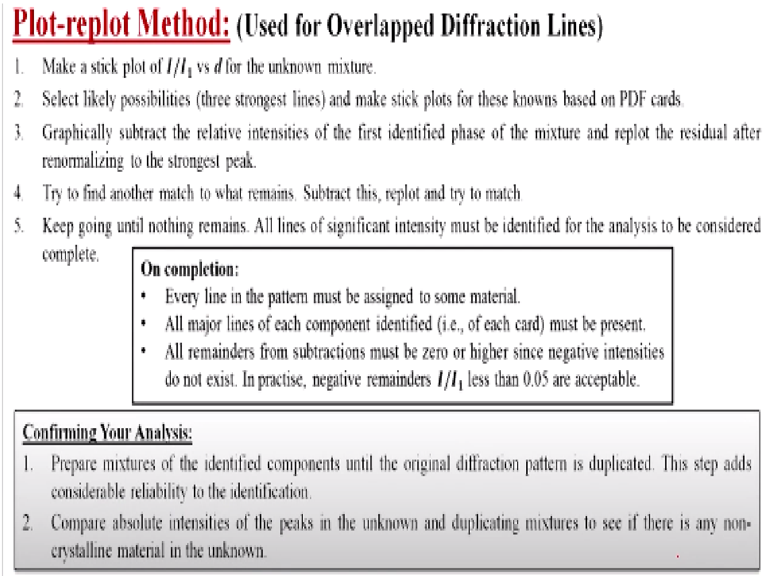

Plot-replot Method: **(Used for Overlapped Diffraction Lines)**

1. Make a stick plot of I/I_1 vs d for the unknown mixture.
2. Select likely possibilities (three strongest lines) and make stick plots for these knowns based on PDF cards.
3. Graphically subtract the relative intensities of the first identified phase of the mixture and replot the residual after renormalizing to the strongest peak.
4. Try to find another match to what remains. Subtract this, replot and try to match
5. Keep going until nothing remains. All lines of significant intensity must be identified for the analysis to be considered complete.

On completion:

- Every line in the pattern must be assigned to some material.
- All major lines of each component identified (i.e., of each card) must be present.
- All remainders from subtractions must be zero or higher since negative intensities do not exist. In practise, negative remainders I/I_1 less than 0.05 are acceptable.

Confirming Your Analysis:

1. Prepare mixtures of the identified components until the original diffraction pattern is duplicated. This step adds considerable reliability to the identification.
2. Compare absolute intensities of the peaks in the unknown and duplicating mixtures to see if there is any non-crystalline material in the unknown.

Next is the plot- Replot method used for the overlapped diffraction line, sometimes it may happen for different materials the line has been overlapped each other then how to distinguish them, make a stick plot of I/I1 versus d for the unknown mixture. Select likely possibilities, three strongest lines and make stick plots for these known's based on PDF cards. Graphically subtract the relative intensities of the first identified phase of the mixture and Replot the residual after renormalizing to the strongest peak.

Try to find another match to what remains, subtract this, replot and try to match. So simple whatever the plot we are getting and after that matching samples pot we are removing, then next matching samples plot 2 we are removing like that we have to make it 0 that there should not be any peak. Keep going until nothing remains all lines of significant intensity must be identified for the analysis to be considered complete.

On completions, every line in the pattern must be assigned to some material all major line of each component identified that is of each card must be present all reminders from subtractions must be 0 or higher since negative intensities do not exist. Impact is negative reminders I/I1 less than 0.05 are acceptable. Confirming your analysis what to do first prepare mixtures of the identified components until the original diffraction pattern is duplicated

This step adds considerable reliability to the identifications. Then second compare the absolute intensities of the peaks in the unknown and duplicating mixtures to see if there is any non crystalline material in the unknown.

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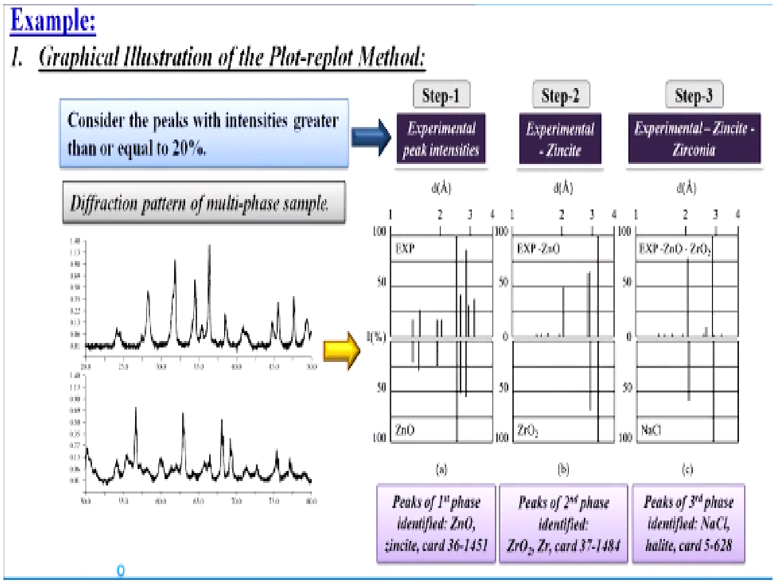

Example:

1. *Graphical Illustration of the Plot-replot Method:*

Consider the peaks with intensities greater than or equal to 20%.

Diffraction pattern of multi-phase sample.

Peaks of 1st phase identified: ZnO, zincite, card 36-1451

Peaks of 2nd phase identified: ZrO_2, Zr, card 37-1484

Peaks of 3rd phase identified: NaCl, halite, card 5-628

So examples, graphical illustrations of the plot-replot method considered the peaks with intensities greater than or equal to 20%. So in this particular case diffraction pattern of multi phase materials where it is mixing experimental peaks intensity is like that so peaks of past phase identified zinc oxide or maybe the zincite card number 361451, so I am subtracting the peak of zinc oxide and then again I am repolting it.

Then peaks of the second phase identified that is zirconium oxide ZrO2 and Zirconia card 371485, so I am eliminating the second then peaks of that third phase identified that is sodium chloride or halite card number 5-628 so after that it will become 0. So first how to do it? Experimental peak intensity is the experimental zincites and then experimental zincite and Zirconia.

So like this way, we will characterize or maybe we will get the information of about the all the materials, numerical illustration of the plot-replot method considered the average d.

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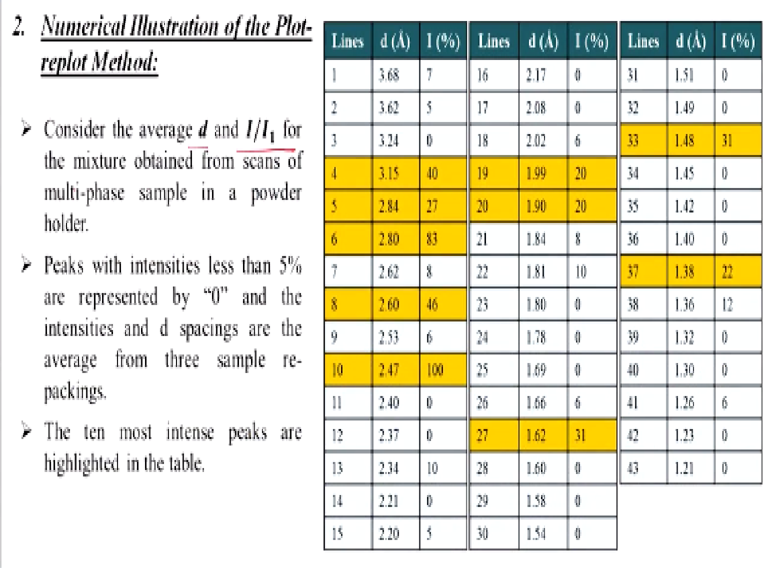

2. *Numerical Illustration of the Plot-replot Method:*

- Consider the average d and I/I_1 for the mixture obtained from scans of multi-phase sample in a powder holder.
- Peaks with intensities less than 5% are represented by "0" and the intensities and d spacings are the average from three sample re-packings.
- The ten most intense peaks are highlighted in the table.

Lines	d (Å)	I (%)
1	3.68	7
2	3.62	5
3	3.24	0
4	3.15	40
5	2.84	27
6	2.80	83
7	2.62	8
8	2.60	46
9	2.53	6
10	2.47	100
11	2.40	0
12	2.37	0
13	2.34	10
14	2.21	0
15	2.20	5
16	2.17	0
17	2.08	0
18	2.02	6
19	1.99	20
20	1.90	20
21	1.84	8
22	1.81	10
23	1.80	0
24	1.78	0
25	1.69	0
26	1.66	6
27	1.62	31
28	1.60	0
29	1.58	0
30	1.54	0
31	1.51	0
32	1.49	0
33	1.48	31
34	1.45	0
35	1.42	0
36	1.40	0
37	1.38	22
38	1.36	12
39	1.32	0
40	1.30	0
41	1.26	6
42	1.23	0
43	1.21	0

And I/I1 for the mixture of 10 from scans of multiple phase samples in a powder holder. Peaks with intensities less than 5% are represented by 0 and then the intensities and d spacing's are the average from three samples re-packing. The ten most intense peaks are highlighted in the table itself, so we will get the number of total 43 lines over there so the most intense peaks has been given like this way so it is 100 high percentage, so that means the d1, d2, d3 up to d10.

And first we have to match d1 to d10 and then after that the rest of the peaks we are going to match.

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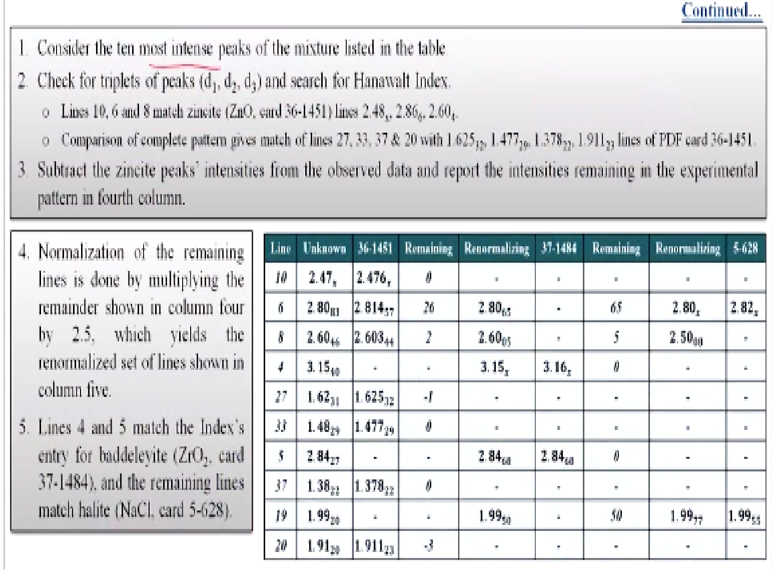

Continued...

1. Consider the ten most intense peaks of the mixture listed in the table.
2. Check for triplets of peaks (d_1, d_2, d_3) and search for Hanawalt Index.
   - Lines 10, 6 and 8 match zincite (ZnO, card 36-1451) lines 2.48_x, 2.86_6, 2.60_4.
   - Comparison of complete pattern gives match of lines 27, 33, 37 & 20 with 1.625_{32}, 1.477_{29}, 1.378_{22}, 1.911_{23} lines of PDF card 36-1451.
3. Subtract the zincite peaks' intensities from the observed data and report the intensities remaining in the experimental pattern in fourth column.
4. Normalization of the remaining lines is done by multiplying the remainder shown in column four by 2.5, which yields the renormalized set of lines shown in column five.
5. Lines 4 and 5 match the Index's entry for baddeleyite (ZrO_2, card 37-1484), and the remaining lines match halite (NaCl, card 5-628).

Line	Unknown	36-1451	Remaining	Renormalizing	37-1484	Remaining	Renormalizing	5-628
10	2.47_x	2.476_x	0	-	-	-	-	-
6	2.80_{81}	2.814_{57}	26	2.80_{65}	-	65	2.80_x	2.82_x
8	2.60_{46}	2.603_{44}	2	2.60_{05}	-	5	2.50_{00}	-
4	3.15_{40}	-	-	3.15_x	3.16_x	0	-	-
27	1.62_{31}	1.625_{32}	-1	-	-	-	-	-
33	1.48_{29}	1.477_{29}	0	-	-	-	-	-
5	2.84_{27}	-	-	2.84_{68}	2.84_{68}	0	-	-
37	1.38_{22}	1.378_{22}	0	-	-	-	-	-
19	1.99_{20}	-	-	1.99_{50}	-	50	1.99_{77}	1.99_{55}
20	1.91_{20}	1.911_{23}	-3	-	-	-	-	-

Consider the 10 most intense peaks of the mixture listed in the table. Check for triplets of peaks like d1, d2, d3 and search for Hanawalt index. Lines 10, 6 and 8 match zincite Zn O card 36-1451 lines 2.48 X, 2.866 and 2.604. So 60%, 40% like that. Comparison of complete pattern gives match of lines 27, 33, 37 and 20 with 1.625 32, 1.47 29, 1.378 22, 1.911 23 lines of PDF card number is 36-1451.

Subtract the zincite peaks intensities from the observed data and report the intensities remaining in the experimental pattern in fourth column. So simple whatever the peaks has been confirmed we have to delete it and then we have to go for the further one. Normalizing of the remaining lines is done by multiplying the reminder shown in column four by 2.5, so simple the column four we are multiplying with the 2.5

Which yields the renormalized set of lines shown in the column five, so line four and five match the index entry for baddeleyite Zirconia oxide card 37-1484, and the remaining line match halite sodium chloride card 5-628.

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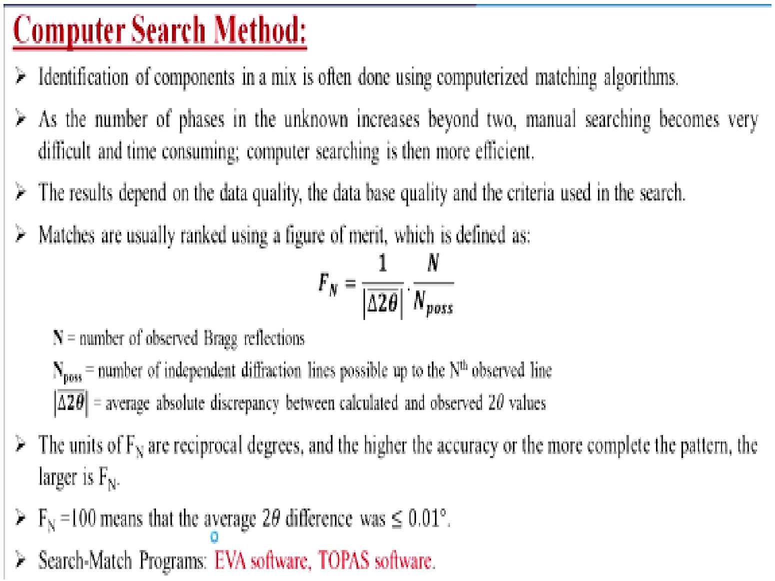

Computer Search Method:

- Identification of components in a mix is often done using computerized matching algorithms.
- As the number of phases in the unknown increases beyond two, manual searching becomes very difficult and time consuming; computer searching is then more efficient.
- The results depend on the data quality, the data base quality and the criteria used in the search.
- Matches are usually ranked using a figure of merit, which is defined as:

$$F_N = \frac{1}{|\overline{\Delta 2\theta}|} \cdot \frac{N}{N_{poss}}$$

N = number of observed Bragg reflections

N_{poss} = number of independent diffraction lines possible up to the N^{th} observed line

$|\overline{\Delta 2\theta}|$ = average absolute discrepancy between calculated and observed 2θ values

- The units of F_N are reciprocal degrees, and the higher the accuracy or the more complete the pattern, the larger is F_N.
- F_N =100 means that the average 2θ difference was ≤ 0.01°.
- Search-Match Programs: EVA software, TOPAS software.

Now this is one is actually the computer search model, so generally the computer how the computer is doing. Identification of components in a mix often is done using computerized matching algorithms. As the number of phases in the unknown increases beyond 2 manual searching becomes very difficult and time consuming. Computer searching is then more efficient, the result depend on the data quality the data based quality and the criteria is used in the search.

Matches are usually ranked using a figure of merit which is defined as F n is equal to 1 by bar Δ2θ into N by N poss. So N is equal to number of observed back reflections N poss. Number of independent reflection lines possible up to the N^{th} observed lines and bar Δ2θ average absolute discrepancy between calculated and observed 2θ values. So here is the vector, so vector bar Δ2θ is equal to average absolute discrepancy between calculated and observed 2θ values.

The units of F n are reciprocal degrees and the higher the accuracy or the more complete the pattern the larger is F n. F n is equal to 100 means that the average 2θ difference was less than is equal to 0.01°. Search match programs like generally we are doing by the EVA software or maybe the TOPAS software.

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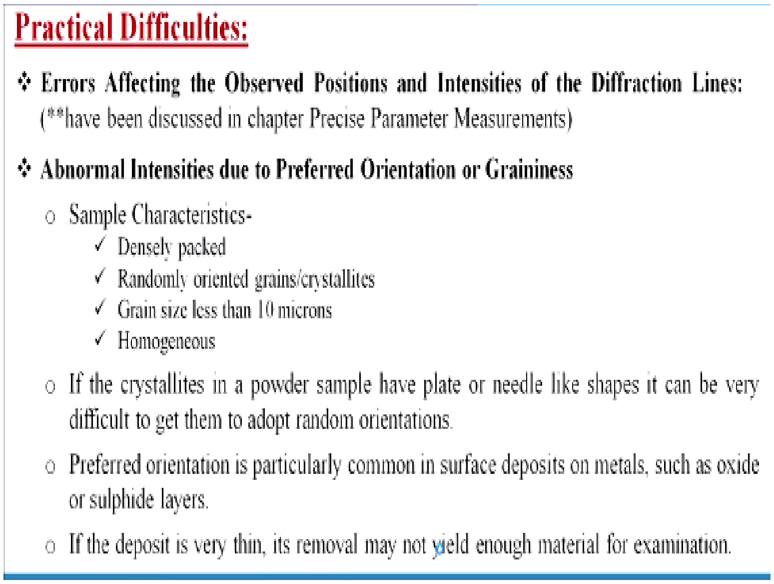

Practical Difficulties:

- ❖ **Errors Affecting the Observed Positions and Intensities of the Diffraction Lines:** (**have been discussed in chapter Precise Parameter Measurements)
- ❖ **Abnormal Intensities due to Preferred Orientation or Graininess**
  - ○ Sample Characteristics-
    - ✓ Densely packed
    - ✓ Randomly oriented grains/crystallites
    - ✓ Grain size less than 10 microns
    - ✓ Homogeneous
  - ○ If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt random orientations.
  - ○ Preferred orientation is particularly common in surface deposits on metals, such as oxide or sulphide layers.
  - ○ If the deposit is very thin, its removal may not yield enough material for examination.

Now there are certain practical difficulties what are those? Errors are affecting the observed positions and the intensities of the diffraction lines have been discussed in chapter precise parameter measurements, so already we have discussed. Abnormal intensities due to preferred orientation or graininess, sample characteristics densely packed, randomly oriented grains or may be the crystallites, grain size less than 10 microns and homogeneous.

If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt the random orientations. That is why we always try to get the orientation of the flat surface. Preferred orientations are particularly common in surface deposits on metals such as oxides or maybe the sulphide layers. If the deposit is very thin it is removal may not yield enough material for examination.

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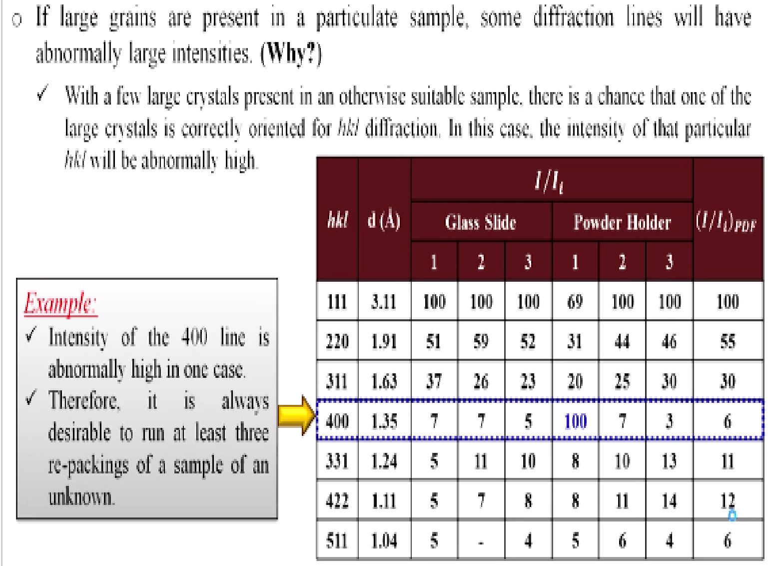

- ○ If large grains are present in a particulate sample, some diffraction lines will have abnormally large intensities. **(Why?)**
  - ✓ With a few large crystals present in an otherwise suitable sample, there is a chance that one of the large crystals is correctly oriented for *hkl* diffraction. In this case, the intensity of that particular *hkl* will be abnormally high.

Example:

- ✓ Intensity of the 400 line is abnormally high in one case.
- ✓ Therefore, it is always desirable to run at least three re-packings of a sample of an unknown.

hkl	d (Å)	I/I_1						$(I/I_1)_{PDF}$
		Glass Slide			Powder Holder			
		1	2	3	1	2	3	
111	3.11	100	100	100	69	100	100	100
220	1.91	51	59	52	31	44	46	55
311	1.63	37	26	23	20	25	30	30
400	1.35	7	7	5	100	7	3	6
331	1.24	5	11	10	8	10	13	11
422	1.11	5	7	8	8	11	14	12
511	1.04	5	-	4	5	6	4	6

If large grains are present in a particulate sample, some diffraction lines will have abnormally large intensities, but the question is why? With a few large crystals present in an otherwise suitable sample there is a chance that one of the large crystals is correctly oriented for HKL diffraction. In this case the intensity of that particular HKL will be abnormally high. In this case you can see that certainly it became 100 otherwise it is 7, 7 5 or may be 7 3 6 but certainly it became the 100 intensity.

So example intensity of the 400 line is abnormally high in one case in this particular case, therefore it is always desirable to run at least three repacking of a sample of an unknown.

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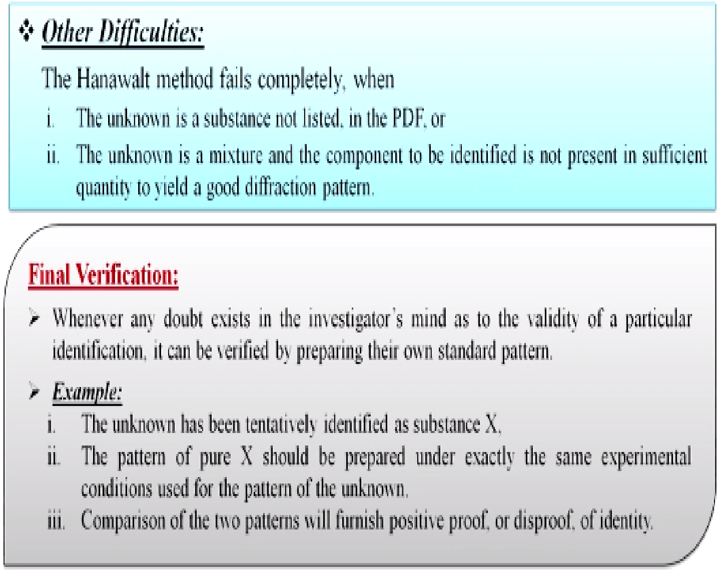

❖ ***Other Difficulties:***

The Hanawalt method fails completely, when

i. The unknown is a substance not listed, in the PDF, or
ii. The unknown is a mixture and the component to be identified is not present in sufficient quantity to yield a good diffraction pattern.

Final Verification:

- Whenever any doubt exists in the investigator's mind as to the validity of a particular identification, it can be verified by preparing their own standard pattern.
- ***Example:***
  i. The unknown has been tentatively identified as substance X.
  ii. The pattern of pure X should be prepared under exactly the same experimental conditions used for the pattern of the unknown.
  iii. Comparison of the two patterns will furnish positive proof, or disproof, of identity.

There are certain other difficulties also the Hanawalt method fails completely when the unknown is a substance not listed in the PDF yes! We don't have any archive. The unknown is a mixture and the component to be identified is not present in sufficient quantity to yield a good diffraction pattern and the final verifications whenever any doubts exist in the investigators mind as to the validity of a particular identification it can be verified by preparing their own standard pattern.

Examples, the unknown has been tentatively identified as substance X, the pattern of pure X should be prepared under exactly the same experimental conditions used for the pattern of the unknown. Comparison of these two patterns will furnish positive proof or disproof of identity. So now we have come to conclusions or maybe we have come to the last part of this particular lecture so we have to summarize the whole lecture. Qualitative analysis by x-ray diffractions is based on the following principles.

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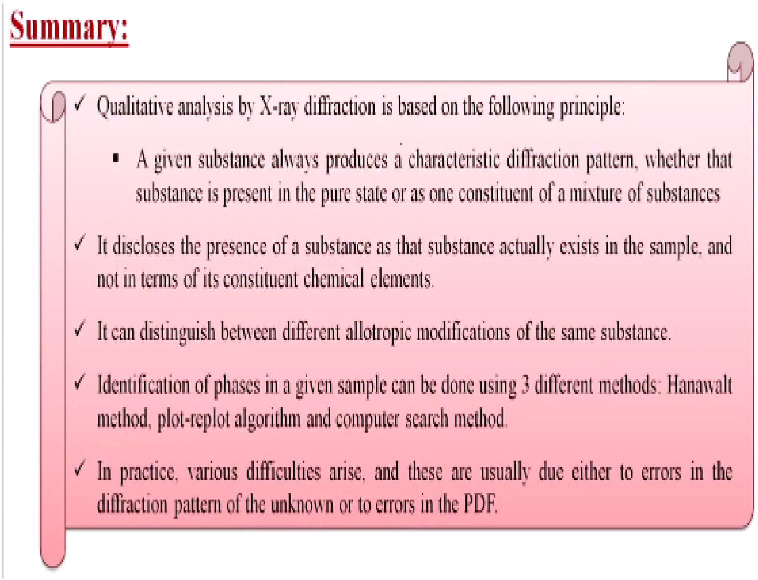

Summary:

- Qualitative analysis by X-ray diffraction is based on the following principle:
  - A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances
- It discloses the presence of a substance as that substance actually exists in the sample, and not in terms of its constituent chemical elements.
- It can distinguish between different allotropic modifications of the same substance.
- Identification of phases in a given sample can be done using 3 different methods: Hanawalt method, plot-replot algorithm and computer search method.
- In practice, various difficulties arise, and these are usually due either to errors in the diffraction pattern of the unknown or to errors in the PDF.

A given substance always produce a characteristics diffraction pattern we know, whether the substance is present in the pure state or as one constituent of a mixture of substances. It discloses the presence of a substance as that substance actually exists in the sample and not in terms of its constituent chemical elements. It can distinguish between different allotropic modifications of the same substance.

Identification of phases in a given sample can be done using three different methods, one is called the Hanawalt method, then next one is called the plot-replot algorithm and the third one is called the computer search method. In practice various difficulties arises and these are usually due to errors in the diffraction pattern of the unknown or to errors in the PDF, Thank You.

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