Characterization of Construction Materials
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Lecture 19
X Ray Diffraction Qualitative Phase Analysis Part 1

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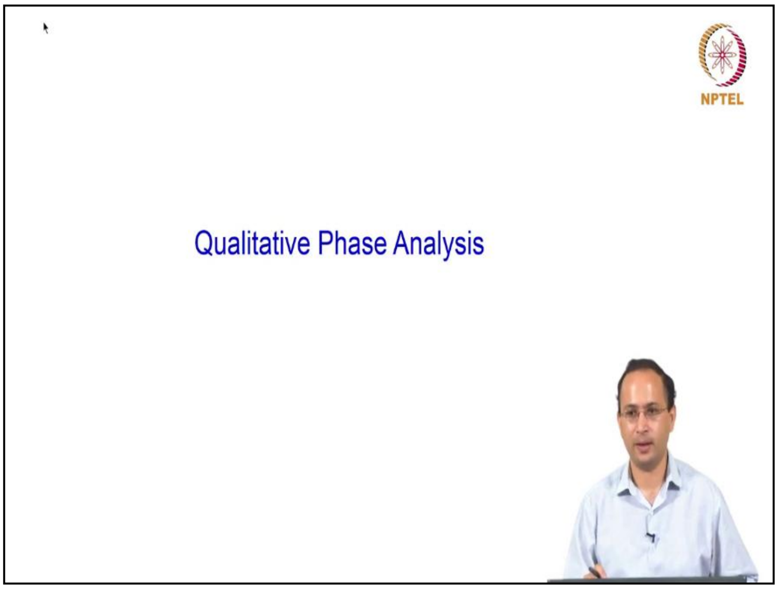

Qualitative Phase Analysis

Now, we will discuss about qualitative phase analysis and how can x-ray diffraction pattern be used for qualitative analysis of the sample. The main idea is to find the phases present in the sample. We do this with the help of database we have which contains information about each phase compared to your pattern obtained.

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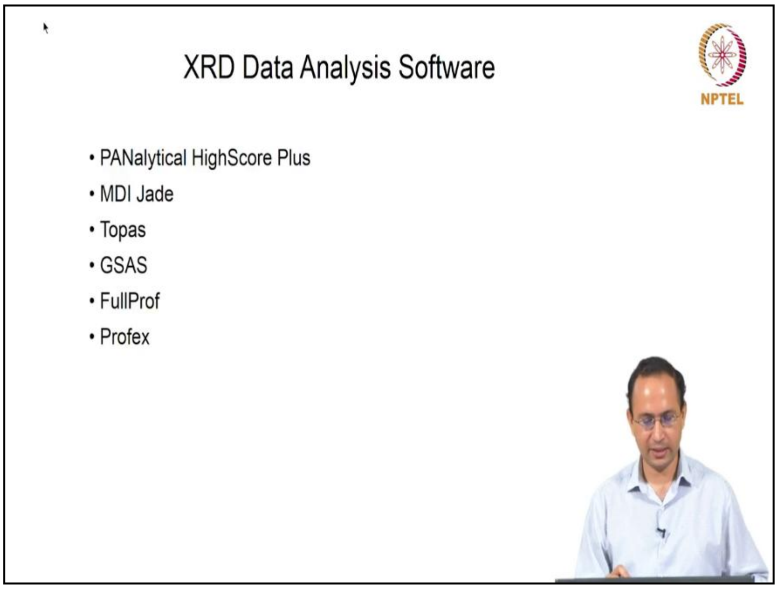

XRD Data Analysis Software

- PANalytical HighScore Plus
- MDI Jade
- Topas
- GSAS
- FullProf
- Profex

There are various software used for this analysis but for the assignment purpose we will use HighScore Plus which is available in our lab.

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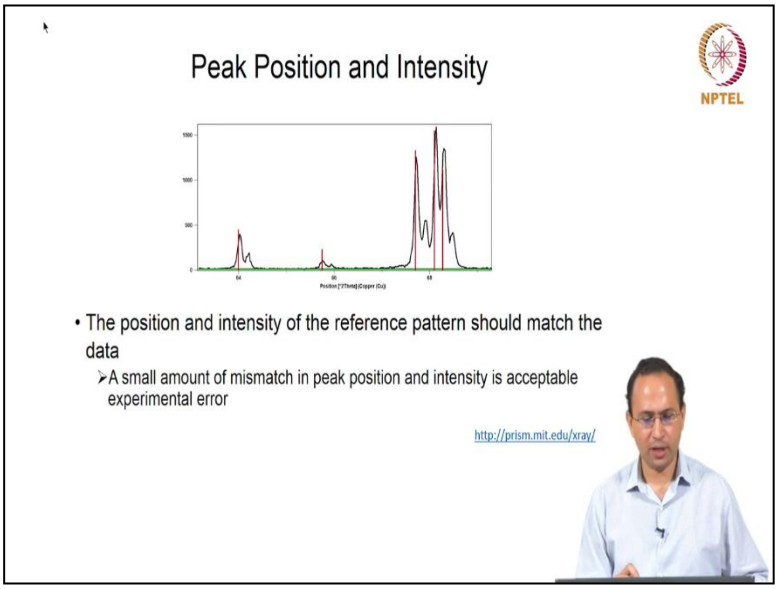

Peak Position and Intensity

- The position and intensity of the reference pattern should match the data
  - ➢A small amount of mismatch in peak position and intensity is acceptable experimental error

http://prism.mit.edu/xray/

So, we were talking about peak position and intensity which is very important. The position and intensity of the reference pattern should match the data.

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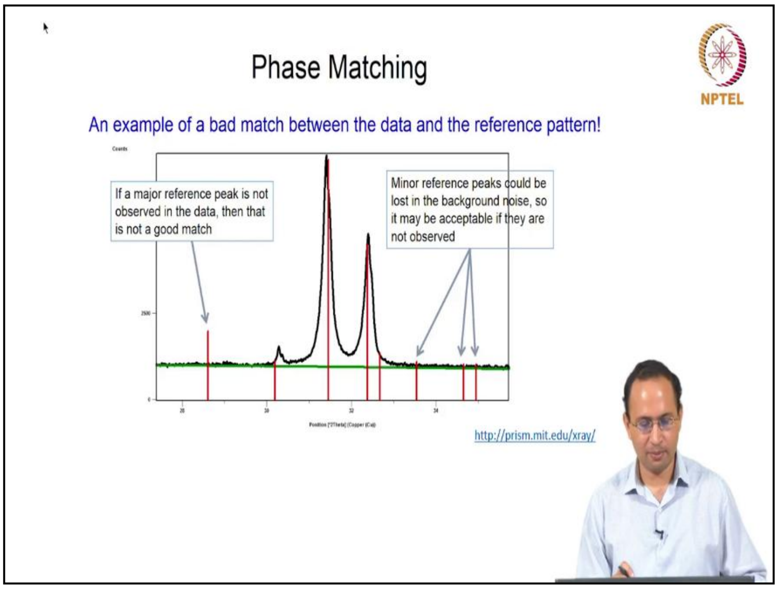

Phase Matching

An example of a bad match between the data and the reference pattern!

If a major reference peak is not observed in the data, then that is not a good match

Minor reference peaks could be lost in the background noise, so it may be acceptable if they are not observed

http://prism.mit.edu/xray/

Here we have an example of a bad match between the data and the reference pattern; we observe although the peaks are matching but there is mismatch in the third strongest peak. This shows there is a problem. These things we always need to check when we do qualitative analysis.

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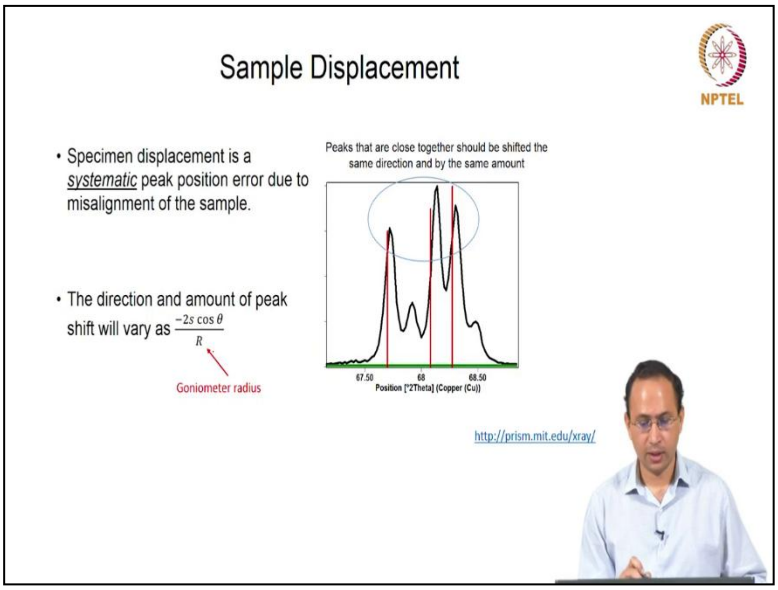

Sample Displacement

- Specimen displacement is a *systematic* peak position error due to misalignment of the sample.
- The direction and amount of peak shift will vary as $\frac{-2s\cos\theta}{R}$

Goniometer radius

Peaks that are close together should be shifted the same direction and by the same amount

http://prism.mit.edu/xray/

Now we will discuss about sample displacement and the reason of its occurrence. As now we are familiar with x-ray diffractometer which basically consist of sample which is like para focusing geometry with X-ray tube and a detector on designated positions. So, the tube and detector will rotate but in some cases sample will also rotate when tube is fixed.

But the idea is that the sample is always at the focus or at the centre of the circle. When there is some displacement or sample is not in the focus so it will cause sample displacement. So, for sample displacement we will observe that the peaks have been shifted by an equal amount. See in this plot given the peaks that are close together should be shifted in the same direction and by the same amount.

So, here we observe that the peak in the pattern is shifted in the same direction. The red one is the reference pattern or the standard obtained from ICDD. We see a constant shift in this case that tells of sample displacement. We can quantify it by using the given formula

$$\frac{-2s\cos\theta}{r}$$

Where s = sample displacement and r is the radius of goniometer.

If you are looking at three strongest peaks and you observe a constant shift then the issue is sample displacement. If you compare 2 different peaks and both peaks are shifted by equal amount that tells you about occurrence of sample displacement.

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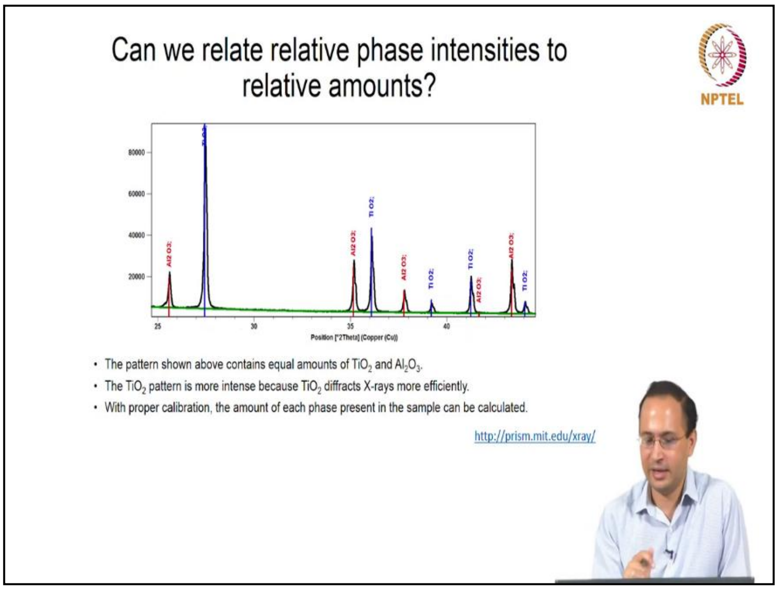

Can we relate relative phase intensities to relative amounts?

- The pattern shown above contains equal amounts of TiO_2 and Al_2O_3.
- The TiO_2 pattern is more intense because TiO_2 diffracts X-rays more efficiently.
- With proper calibration, the amount of each phase present in the sample can be calculated.

http://prism.mit.edu/xray/

Now, the question comes once we have identified the phases; can it be related to the relative phase intensity of relative amounts. For an instance we take the case here for sample made of Al_2O_3 and TiO_2. Can you relate this two relative phase intensity of relative amounts is the main question that arises? It is not possible to relate your phase intensities to phase amounts by just looking at the plot.

In actual we know that the phase composition is 50% TiO_2 and 50% Al_2O_3 but we cannot predict this by just looking at plot as the TiO_2 pattern is more intense. The TiO_2 pattern is more intense because it deflects x rays more efficiently as compared to Al_2O_3. It depends on type of phase we are looking at. We cannot just by looking at intensities predict amounts.

With proper calibration the amount of each phase present in the sample can be calculated. We will have to do proper calibration for that. When we want to do quantitative analysis; we will have to do some calibration and we will talk about it later. Now the question comes we do not know how to do quantitative phase analysis after recognising the major peaks present in our sample.

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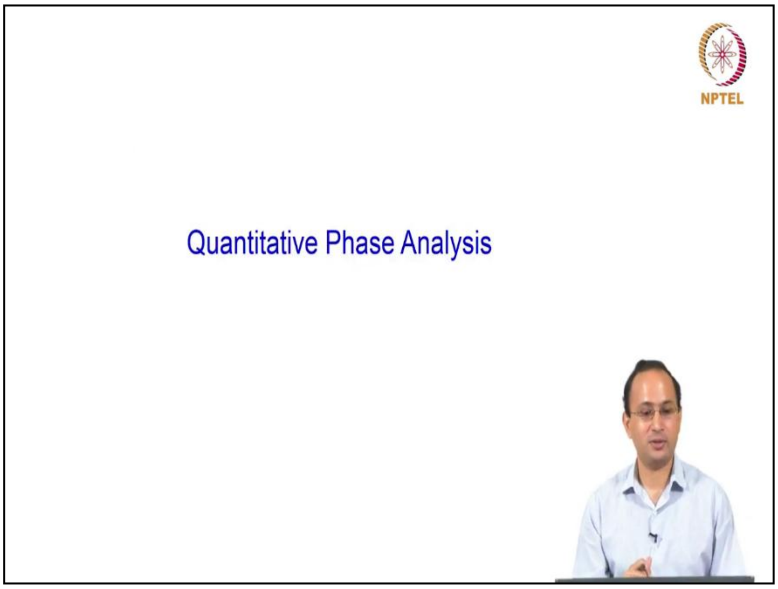

Quantitative Phase Analysis

Obliviously the second question comes how do we quantify the phase that is very important right when you are talking about phase analysis like once you have identified the phases it is very important to know how much?

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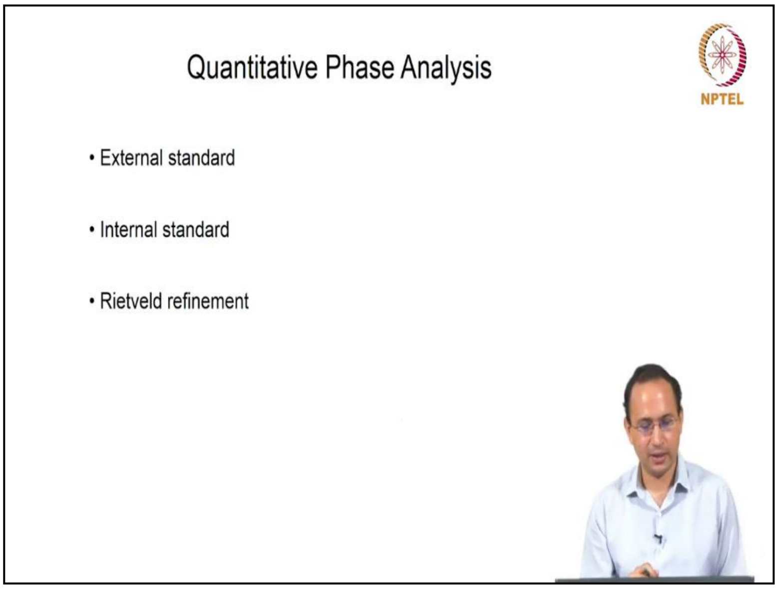

Quantitative Phase Analysis

- External standard
- Internal standard
- Rietveld refinement

There are different ways to do quantitative phase analysis. We will start discussion with external standards then internal standards and in last we will talk about Rietveld refinement. Rietveld refinement is most commonly used these days and is quite popular.

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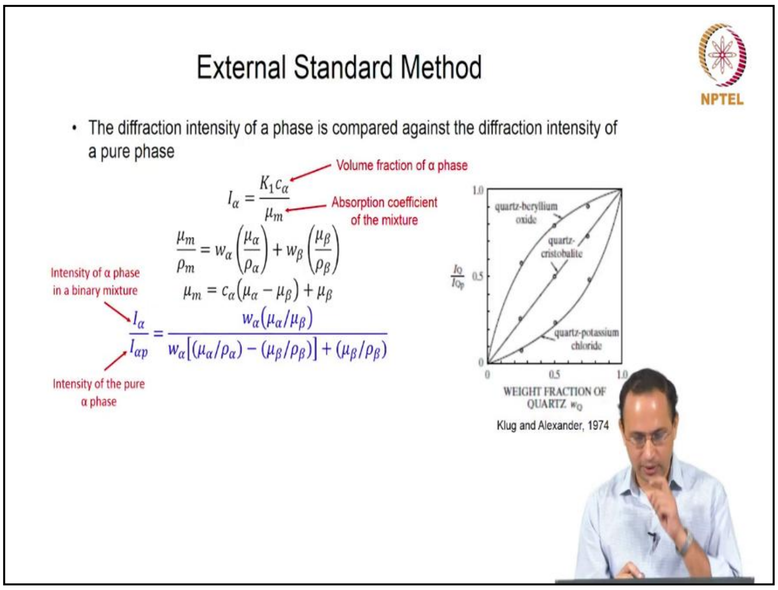

External Standard Method

- The diffraction intensity of a phase is compared against the diffraction intensity of a pure phase

Volume fraction of α phase

Absorption coefficient of the mixture

$$I_\alpha = \frac{K_1 c_\alpha}{\mu_m}$$

$$\frac{\mu_m}{\rho_m} = w_\alpha\left(\frac{\mu_\alpha}{\rho_\alpha}\right) + w_\beta\left(\frac{\mu_\beta}{\rho_\beta}\right)$$

$$\mu_m = c_\alpha(\mu_\alpha - \mu_\beta) + \mu_\beta$$

Intensity of α phase in a binary mixture

$$\frac{I_\alpha}{I_{\alpha p}} = \frac{w_\alpha(\mu_\alpha/\mu_\beta)}{w_\alpha[(\mu_\alpha/\rho_\alpha) - (\mu_\beta/\rho_\beta)] + (\mu_\beta/\rho_\beta)}$$

Intensity of the pure α phase

Klug and Alexander, 1974

In external method, the diffraction intensity of phase is compared against the diffraction intensity of a pure phase. Suppose we consider mixture of α and β. Now you are comparing the intensity in your sample like α intensity to the intensity of α in pure α phase.

Suppose if we do x-ray diffraction for pure α; we get a lot of peaks and look at the strongest peak. This is about comparing the intensity of the particular hkl at pure α phase versus intensity of hkl in the mixture α phase. The famous equation to calculate the intensity of diffracted beam

$$\mathrm{I} = \mathrm{F}^2 p\ L\ A\ T$$

Here we know F is structure factor, p is multiplicity factor, L is Lorentz polarization factor, A is the absorption factor and T is temperature factor.

$$\mathrm{I} = \mathrm{F}^2\ p\ L\left(\frac{e^{-2\mu}}{2\mu}\right)$$

So here absorption factor $\mathrm{A} = \left(\frac{1}{2\mu}\right)$

The absorption will depend on the absorption coefficient. If you have very high absorption that means the intensity of the diffracted beam is very low.

For a particular phase α; as we are talking about binary system where we have α and β and want to determine the quantities of both. Iα can be written as

$$\mathrm{I\alpha} = \frac{\mathrm{K1.C\alpha}}{\mu\mathrm{m}}$$

Where Iα is the intensity of the α phase, Cα is the volume fraction of α phase and μ_m is the absorption coefficient of the mixture. For Cα equal to 1 we will get the intensity equal to that of the pure phase. K_1 will be constant as we are talking about 1 hkl or one plane and strongest peak in this context.

These equations below show how we relate the absorption coefficient of the mixture to the volume fraction of each phase and to the mass absorption coefficient of each phase. Equation below gives nothing but the weighted average of μ_m over ρ_m

$$\frac{\mu m}{\rho m} = W\alpha\ \left(\frac{\mu\alpha}{\rho\alpha}\right) + W\beta\ \left(\frac{\mu\beta}{\rho\beta}\right)$$

Wα is the weight of α phase and Wβ represents the weight of the β phase in the binary mixture. μ_α and μ_β are the absorption coefficient of α and β phases in the mixture respectively.

The equation below gives the relation of absorption coefficient of the mixture and volume fraction of α phase

$$\mu m = C\alpha(\mu\alpha - \mu\beta) + \mu\beta$$

The relationship between intensity of α phase in a binary mixture (Iα) and the intensity of the pure α phase (Iαp) is given as follows

$$\frac{I\alpha}{I\alpha p} = \frac{W\alpha\left(\frac{\mu\alpha}{\mu\beta}\right)}{W\alpha\left[\left(\frac{\mu\alpha}{\rho\alpha}\right) - \left(\frac{\mu\beta}{\rho\beta}\right)\right] + \left(\frac{\mu\beta}{\rho\beta}\right)}$$

If you look at the plot, the lower most curve was derived for Quartz Potassium Chloride mixture. So, quartz here will be the external standard mixture. So, we can see in the plot that we can vary the amount of quartz. So, depending on the weight fraction of quartz, we can see the relationship of Iα / Iαp we get the data points.

It is quite visible that the curve is not a linear one. Suppose for a binary mixture the absorption coefficients for both the phases are same then it will become directly proportional to Wα. Then the curve will become linear so it highly depends on the values of absorption coefficient of the phases present. So, if you have developed these kind of calibration curve as shown; depending on the intensity and the ratio we can calculate the weight fraction..

If you know the weight fraction of α; you can determine the same for β using external standard method. In simpler terms to conclude, the external standard is used where we are comparing the intensity of phase against the diffraction intensity of pure phase.

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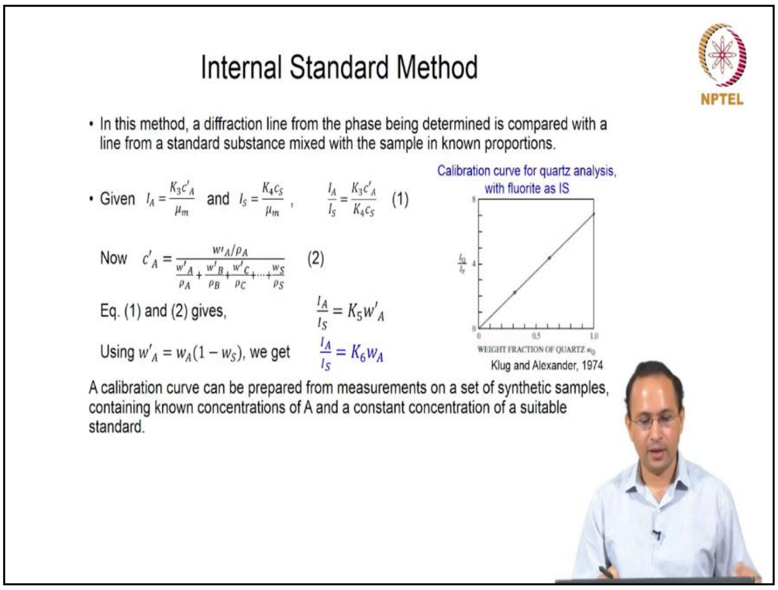

Internal Standard Method

- In this method, a diffraction line from the phase being determined is compared with a line from a standard substance mixed with the sample in known proportions.
- Given $I_A = \frac{K_3 c'_A}{\mu_m}$ and $I_S = \frac{K_4 c_S}{\mu_m}$, $\frac{I_A}{I_S} = \frac{K_3 c'_A}{K_4 c_S}$ (1)

Now $c'_A = \frac{w'_A/\rho_A}{\frac{w'_A}{\rho_A} + \frac{w'_B}{\rho_B} + \frac{w'_C}{\rho_C} + \dots + \frac{w_S}{\rho_S}}$ (2)

Eq. (1) and (2) gives, $\frac{I_A}{I_S} = K_5 w'_A$

Using $w'_A = w_A(1 - w_S)$, we get $\frac{I_A}{I_S} = K_6 w_A$

A calibration curve can be prepared from measurements on a set of synthetic samples, containing known concentrations of A and a constant concentration of a suitable standard.

Calibration curve for quartz analysis, with fluorite as IS

Klug and Alexander, 1974

Now coming onto internal standard method so as name suggest it is the standard used internally. We use this method to spike the samples. So here we can add substance in to the sample which is a clear difference between external and internal. So here we are mixing standard with your sample. So, in this method a diffraction line from the phase being determined is compared with a line from a standard substance mixed with the sample in know proportions.

You know how much you are adding in to the sample and the standard both. You have a sample suppose that is $\alpha + \beta$ and you know you are using a standard as for example 10% of the sample. So, you added 10% of your sample. You know the 10% but it is mixed with sample that is why it is called internal standard. So again we come back to the intensity equation which is very important and now let us say for A phase as mentioned below.

$$IA = \frac{[K3.C'A]}{\mu m}$$

So here I_A is the intensity of A phase, K_3 is the constant and C'_A is the volume fraction of A phase.

For a mixture of 4 phases A+B+C+D we add S (predetermined quantity). For this we want to calculate W_A W_B W_C and W_D which are the weight fractions of different phases present in the mixture.

For calculating the above, we are adding standard with ABCD. Now if we have to focus on the intensity of the line, we are talking about the strongest line. I_A is not just the height but the integrated intensity. So, in this calculation where we are using intensity that is integrated intensity which is the area under the curve. You know that you have this peak, calculate the area under the curve that will give you integrated intensity.

Now if we write for Is which is the intensity for strongest peak of standard, so it will be

$$\mathrm{Is} = \frac{\mathrm{K4.Cs}}{\mu \mathrm{m}}$$

Where Cs is the volume fraction of the standard in the A+B+C+D mixture. The ratio of I_A to I_S is given as follows:

$$\frac{\mathrm{IA}}{\mathrm{Is}} = \frac{K3.C'A}{K4.Cs}$$

C'_A is the volume fraction which volume of A over total volume of the mixture. Volume of A will be weight of A over density of A. We are using the prime for notation as the mixture is now changed to A + B + C + D + S.

If we combine the above two equations we get

$$\frac{\mathrm{IA}}{\mathrm{Is}} = K5.W'A$$

Where $W'_A = W_A(1\text{-}Ws)$

Hence we get on simple substitution

$$\frac{\mathrm{IA}}{\mathrm{Is}} = \mathrm{K6.Wa}$$

And basically you get a basic relationship in terms of W prime A the weight fraction A. And this weight fraction A it depends on this is equal to WA times 1 - WS that means if WS is 0 here W prime is WA. When there is no standard your W prime A will become W and when your WS is equal to 1 then 0. But WS you know the how much internal standard you have used. So, when you replace this W prime with WA time 1 – WS you get constant time with WA you know all the other things.

So, now the above relationship tells that it is the linear relationship as visible from the plot. So this is the calibration curve for the quartz where fluorite is used as internal standard. The plot shows the variation in I_Q over I_F as the weight fraction of the quartz varies. So by this you can calculate the quantity of quartz in your sample by using fluorite as internal standard.

A calibration curve can be prepared from measurements on a set of synthetic samples containing known conservation of A and a constant concentration of a suitable standard. In this case we see it as fluoride. Again the intensity we are using here is integrated intensity which is area under the curve.