



Analytical Methods for Materials

Laboratory Module #7

Quantitative Phase Analysis of Powder Mixtures

Suggested Reading

- C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 223-236.
- B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, (Prentice-Hall, Upper Saddle River, NJ, 2001), Ch. 12, pages 347-362.
- Y. Waseda, E. Matsubara, and K. Shinoda, *X-ray Diffraction Crystallography*, (Springer, New York, NY, 2011), Ch. 4, pages 121-123, 155-158.

Objectives

- Upon completion of this module, the student will be able to determine the amount of a crystalline phase that is present in a multiphase material.

Background

- X-ray intensity depends on the amount (i.e., concentration) of the phase that is present in a given sample.
- The concentration relationship is nonlinear. This is because diffracted intensity depends on absorption by the mixture, which also depends on composition.

Integrated Intensity

$$I_{hkl} = \left(\frac{I_o A \lambda^3}{32 \pi r} \right) \left[\left(\frac{\mu_o}{4 \pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{V^2} \right) \left[|F_{hkl}|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right)$$

I_o = intensity of incident beam ($\text{J s}^{-1} \text{m}^{-2}$);

A = area of incident beam (m^2);

λ = wavelength of incident beam (m);

r = radius of diffractometer circle (m);

$\mu_o = 4\pi \times 10^{-1} \text{ (m kg C}^{-2}\text{)}$;

e = charge of electron (C);

μ = linear absorption coefficient (m^{-1})

m = mass of electron (kg);

V = volume of unit cell (m^3);

F_{hkl} = structure factor for reflection;

p = multiplicity factor

θ = Bragg angle;

e^{-2M} = temperature factor;

This equation applies for single phase polycrystalline specimens with randomly oriented grains.

Must be modified for phase mixtures.

Intensity of mixtures

- Multiply the right side of the equation by the volume fraction of that particular phase in the mixture.
- For a mixture $\alpha+\beta$, volume fraction of $\alpha = c_\alpha$.

$$\therefore I_\alpha = \frac{(\text{constant})c_\alpha}{\mu_{mix}} = \frac{K_1 c_\alpha}{\mu_{mix}}$$

- We can re-write this expression in terms of mass absorption coefficients as:

$$\left(\frac{\mu}{\rho}\right)_{mix} = w_\alpha \left(\frac{\mu}{\rho}\right)_\alpha + w_\beta \left(\frac{\mu}{\rho}\right)_\beta$$

Weight % α Weight % β

Intensity of Mixtures – cont'd

Weight of α phase in mixture = $w_\alpha \rho_{mix}$

Volume of α phase in mixture = $c_\alpha = \frac{w_\alpha \rho_{mix}}{\rho_\alpha}$

Weight of β phase in mixture = $w_\beta \rho_{mix}$

Volume of β phase in mixture = $c_\beta = \frac{w_\beta \rho_{mix}}{\rho_\beta}$

From these expressions we can develop expressions for I_α and I_β .

- For example,

$$I_\alpha = \frac{K_1}{\mu_{mix}} \frac{w_\alpha}{\rho_\alpha} \rho_{mix} = \frac{K_1 w_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho} \right)_{mix}}$$

Determine chemistry (*i.e.*, w_α or c_α) from the ratio $I_\alpha / I_{(reference\ peak)}$.

Methods of analysis

1. External standard method (ref. peak from pure α);
2. Direct comparison method (ref. peak from another phase in mixture);

Relatively simple. What we will do in lab.
3. Internal standard method (ref. peak from a foreign material added to specimen).

This method is most widely used in industry due to its simplicity

External Standard Method

$$I_{\alpha,pure} = \frac{K_1}{\mu_{\alpha}}$$

- If we divide I_{α} by $I_{\alpha,pure}$, we get:

$$\frac{I_{\alpha}}{I_{\alpha,pure}} = \frac{K_1 (\mu/\rho)_{\alpha} \mu_{\alpha}}{(\mu/\rho)_{mix} K_1} = \frac{w_{\alpha} (\mu/\rho)_{\alpha}}{(\mu/\rho)_{\alpha,mix}}$$

- Provided we know the mass absorption coefficients for each phase, we can calculate w_{α} from the equation above
- Quite often we don't know the mass absorption coefficients. In those instances we plot a calibration curve:

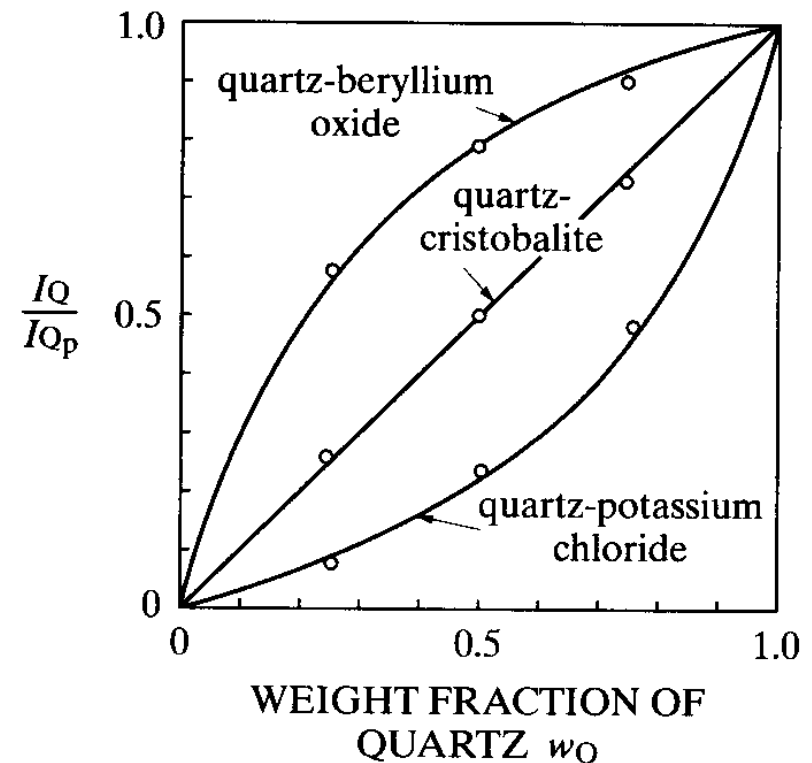
External Standard Method – cont'd

For mixtures with known compositions:

$$\text{Plot } \frac{I_{\alpha}}{I_{\alpha, \text{pure}}} \text{ versus } w_{\alpha}$$

From Cullity and Stock, 3rd edition

Figure 12-1 Diffractometer measurements made with Cu $K\alpha$ radiation on binary mixtures. I_Q is the intensity of the reflection from the $d = 3.34 \text{ \AA}$ planes of quartz in a mixture. I_0 is the intensity of the same reflection from pure quartz. Alexander and Klug [12.5].



From these plots we can determine w_{α} for any given value of $(I_{\alpha}/I_{\alpha, \text{pure}})$

External Standard Method – cont'd

- Must have pure α phase available as reference (not always possible).
- Must measure I_{α} and $I_{\alpha,\text{pure}}$ under identical conditions.
- As you can see, variation with w_{α} is usually non-linear.

Direct Comparison Method

- This method does not require a sample of a pure version of a phase whose composition is being determined.
- The required reference line will come from another phase in the same specimen.
- Method has been commonly used to measure the amount of retained austenite in steel*.

*B.L. Averbach and M. Cohen, *Trans. AIME*, 176 (1948) 401

Direct Comparison Method – cont'd

- From basic intensity equation:

$$I_{hkl} = \left(\frac{I_o A \lambda^3}{32 \pi r} \right) \left[\left(\frac{\mu_o}{4 \pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{V^2} \right) \left[|F_{hkl}|^2 P \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right)$$

Unit cell volume



- Let $K_2 = \left(\frac{I_o A \lambda^3}{32 \pi r} \right) \left[\left(\frac{\mu_o}{4 \pi} \right)^2 \frac{e^4}{m^2} \right]$

$$R = \left(\frac{1}{V^2} \right) \left[|F_{hkl}|^2 P \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] (e^{-2M})$$

- The diffracted intensity becomes: $I = \frac{K_2 R}{2\mu}$

Direct Comparison Method – cont'd

- Re-write the intensity in terms of the phases present, we get:

$$I_{\alpha} = \frac{K_2 R_{\alpha} c_{\alpha}}{2\mu_{mix}}$$

$$I_{\beta} = \frac{K_2 R_{\beta} c_{\beta}}{2\mu_{mix}}$$

- If we take the ratio I_{α}/I_{β} , we eliminate K_2 and μ_{mix} .

$$\frac{I_{\alpha}}{I_{\beta}} = \frac{R_{\alpha} c_{\alpha}}{R_{\beta} c_{\beta}}$$

Once c_{α}/c_{β} is known, we can find either c_{α} or c_{β} .
Remember $c_{\alpha} + c_{\beta} = 1$.

Direct Comparison Method – cont'd

- A few precautions:
 - The α and β peaks should not overlap.
 - Unit cell volume, V , should be calculated from observed lattice parameters, not those from ICDD cards.
 - Integrated intensity (calculated or measured) should be used as opposed to peak heights.

Internal Standard Method

- Mix known amount of a standard to known amount of phase mixture (i.e., specimen).
- The specimen is assumed to be a mixture of phases (i.e., $\alpha+\beta+\gamma+\delta+\dots$).

c_α = volume fraction of α in mixture;

c'_α = volume fraction of α in new mixture (i.e., mix + std.);

c_s = volume fraction of standard in new mixture;

- Borrowing from the last method, we obtain intensity equations for each phase.

Internal Standard Method – cont'd

$$I_{\alpha} = \frac{K_3 c'_{\alpha}}{\mu_{mix}}$$

$$I_{\beta} = \frac{K_4 c_S}{\mu_{mix}}$$

- Once again, if we take ratios of peaks we get:

$$\frac{I_{\alpha}}{I_{\beta}} = \frac{K_3 c'_{\alpha}}{\mu_{mix}} \frac{\mu_{mix}}{K_4 c_S} = \frac{K_3 c'_{\alpha}}{K_4 c_S}$$

from which we can develop expressions for c_S , c'_{α} and the other phases. For example:

$$c'_{\alpha} = \frac{(w'_{\alpha} / \rho_{\alpha})}{(w'_{\alpha} / \rho_{\alpha} + w'_{\beta} / \rho_{\beta} + w'_{\gamma} / \rho_{\gamma} + w'_{\delta} / \rho_{\delta} + \dots + w'_S / \rho_S)}$$

Internal Standard Method – cont'd

$$\frac{c'_\alpha}{c_S} = \frac{w'_\alpha \rho_S}{\rho_\alpha w_S}$$

$$\frac{I_\alpha}{I_S} = \frac{K_3}{K_4} \frac{\rho_S}{\rho_\alpha w_S} w'_\alpha = K_5 w'_\alpha$$

$$w'_\alpha = w_\alpha (1 - w_S) = w_\alpha (\text{constant})$$

∴

$$\frac{I_\alpha}{I_S} = K_6 w_\alpha$$

Since this relationship is linear, we can easily develop a calibration curve.

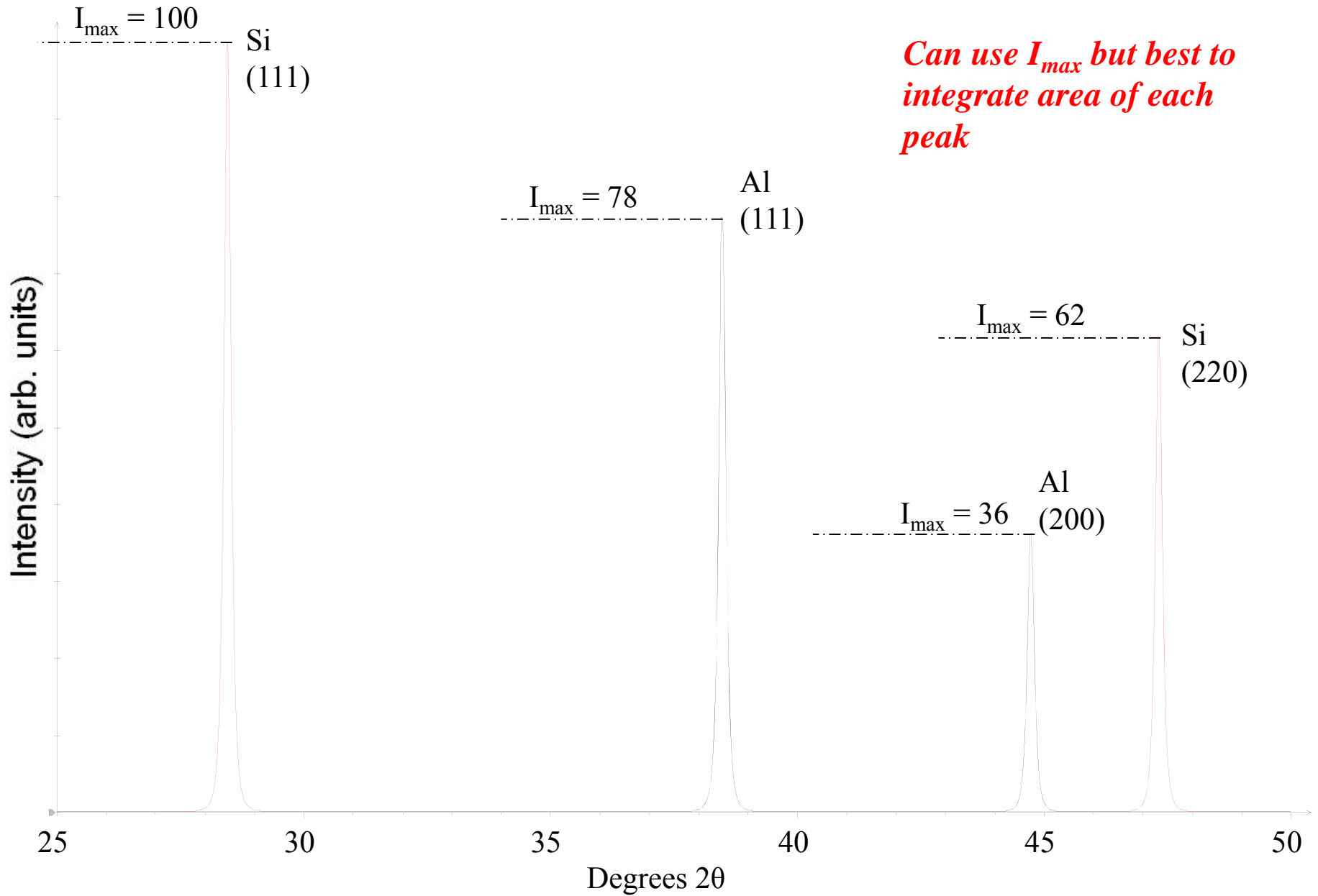
CONFUSED?

Me too!

Let's take a look at the worked example
provided by Suryanarayana and Norton
(pp. 230-232)

However, we'll use a simulated XRD pattern

X-ray diffraction pattern of an Al-Si mixture



Worked example of the direct comparison method

From the XRD pattern, the peaks have been indexed as $(111)_{Al}$, $(111)_{Si}$, $(200)_{Al}$ and $(220)_{Si}$. The integrated intensities and R values must be determined for each reflection. The integrated intensities are the peak areas. Can use software for this.

ALUMINUM

Peak No.	2θ	θ	$\sin^2\theta$	$1*\sin^2\theta/\sin^2\theta_{min}$	$2*\sin^2\theta/\sin^2\theta_{min}$	$3*\sin^2\theta/\sin^2\theta_{min}$	$h^2+k^2+l^2$	h	k	l	a (nm)	$\sin\theta/\lambda$	f_{Al}	F^2	p	LPF	Intensity	R
1	38.52	19.3	0.1088	1.0	2.0	3.0	3	1	1	1	0.4044699	0.2141	9	1290.2	8	15.70	162,006	36,961,185
2	44.76	22.4	0.1450	1.3	2.7	4.0	4	2	0	0	0.404615	0.2471	8.6	1172.4	6	11.22	78,932	18,008,234

VOLUME = 0.0662

SILICON

Peak No.	2θ	θ	$\sin^2\theta$	$1*\sin^2\theta/\sin^2\theta_{min}$	$2*\sin^2\theta/\sin^2\theta_{min}$	$3*\sin^2\theta/\sin^2\theta_{min}$	$h^2+k^2+l^2$	h	k	l	a (nm)	$\sin\theta/\lambda$	f_{Si}	F^2	p	LPF	Intensity	R
1	28.41	14.2	0.0602	0.6	1.1	1.7	3	1	1	1	0.5436876	0.1593	11	3650.0	8	30.38	887,181	34,561,549
2	47.35	23.7	0.1612	1.5	3.0	4.4	8	2	2	0	0.5425709	0.2607	8.8	4944.9	12	9.88	586,286	22,839,693

VOLUME = 0.1602

These numbers come from Suryanarayana and Norton's book.

The numbers for my simulated pattern will be slightly different (next page)

Integrated intensity of the $(111)_{Al}$ peak, $I_{Al,(111)} = 231.0$

R value for $(111)_{Al}$ peak, $R_{Al,(111)} = 36,961,185$

Integrated intensity of the $(200)_{Al}$ peak, $I_{Al,(200)} = 110.6$

R value for $(200)_{Al}$ peak, $R_{Al,(200)} = 18,008,234$

Integrated intensity of the $(111)_{Si}$ peak, $I_{Si,(111)} = 195.2$

R value for $(111)_{Si}$ peak, $R_{Si,(111)} = 34,561,549$

Integrated intensity of the $(220)_{Si}$ peak, $I_{Si,(220)} = 110.4$

R value for $(220)_{Si}$ peak, $R_{Si,(220)} = 23,078,484$

Integrated area of experimental peak (NOT CALCULATED)

RECALL: Integrated Intensity

$$I_{hkl} = \left(\frac{I_o A \lambda^3}{32\pi r} \right) \left[\left(\frac{\mu_o}{4\pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{V^2} \right) \left[|F_{hkl}|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right)$$

I_o = intensity of incident beam ($\text{J s}^{-1} \text{m}^{-2}$);

A = area of incident beam (m^2);

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$\mu_o = 4\pi \times 10^{-1} \text{ (m kg C}^{-2}\text{)}$;

e = charge of electron (C);

μ = linear absorption coefficient (m^{-1})

m = mass of electron (kg);

V = volume of unit cell (m^3);

F_{hkl} = structure factor for reflection;

p = multiplicity factor

θ = Bragg angle;

e^{-2M} = temperature factor;

The **blue** items are constant or difficult to measure

The red items can be measured and/or calculated

We can ignore the temperature factor since we measured at RT

Worked example of the direct comparison method

From the XRD pattern, the peaks have been indexed as $(111)_{Al}$, $(111)_{Si}$, $(200)_{Al}$ and $(220)_{Si}$. The integrated intensities and R values must be determined for each reflection. The integrated intensities are the peak areas. Can use software for this.

ALUMINUM

Peak No.	2θ	θ	sin ² θ	1*sin ² θ/sin ² θ _{min}	2*sin ² θ/sin ² θ _{min}	3*sin ² θ/sin ² θ _{min}	h ² +k ² +l ²	h	k	l	a (nm)	sinθ/λ	f _{Al}	F ²	p	LPF	Intensity	R
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SILICON

Peak No.	2θ	θ	sin ² θ	1*sin ² θ/sin ² θ _{min}	2*sin ² θ/sin ² θ _{min}	3*sin ² θ/sin ² θ _{min}	h ² +k ² +l ²	h	k	l	a (nm)	sinθ/λ	f _{Si}	F ²	p	LPF	Intensity	R
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R value for $(220)_{Si}$ peak, $R_{Si,(220)} = 23,078,484$

Integrated area of
experimental peak
(NOT CALCULATED)

The numbers for my
simulated pattern
will be slightly
different (next
page)

$$\frac{c_{Al}}{c_{Si}} = \frac{I_{Al} R_{Si}}{I_{Si} R_{Al}}$$

∴ for $(111)_{Al}$ and $(111)_{Si}$

$$\frac{c_{Al}}{c_{Si}} = \frac{231.0}{195.2} \times \frac{34,561,549}{36,961,185} = 1.106$$

and for $(200)_{Al}$ and $(220)_{Si}$

$$\frac{c_{Al}}{c_{Si}} = \frac{110.6}{110.4} \times \frac{23,078,484}{18,008,234} = 1.284$$

Since $c_{Al} + c_{Si} = 1$, $c_{Si} = 0.474$ for the $(111)_{Al}$ and $(111)_{Si}$ combination and $c_{Si} = 0.438$ for the $(200)_{Al}$ and $(220)_{Si}$ combination.

From this the average volume fraction of Si in the mixture is 0.456 or 45.6 vol. %.
The volume fraction of Al is 0.544 or 54.4 vol.%.

Final Comments

- This method really works. You should try it out by working out the example yourself or doing the exercise in Experimental Module 7 in S&N.
- You will be expected to do this in your Final Project.

Learning Objective

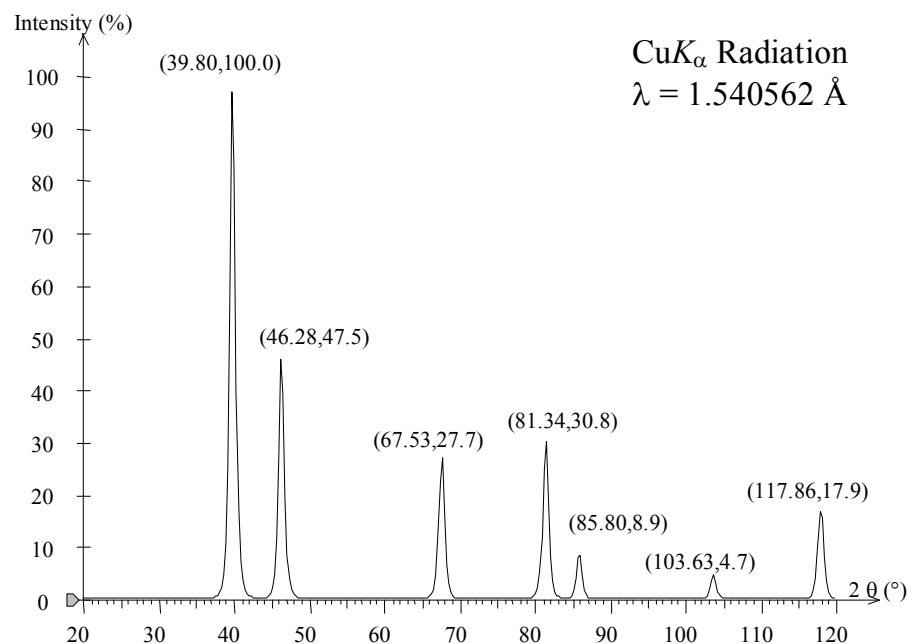
- Upon completion of this module, the student will be able to accurately identify an unknown specimen using the ICDD search manuals.
- Upon completion of this module, the student will know how ICDD search-match software works.

Introduction

- In engineering practice, it is highly likely that you will be called upon to identify an unknown material.
- Where this is critical
 - Failure analysis
 - Reverse engineering
 - Development of new alloys
 - Etc...

How is it done?

1. Collect an XRD pattern and calculate the d -spacing for each reflection.



$$n\lambda = 2d \sin \theta$$

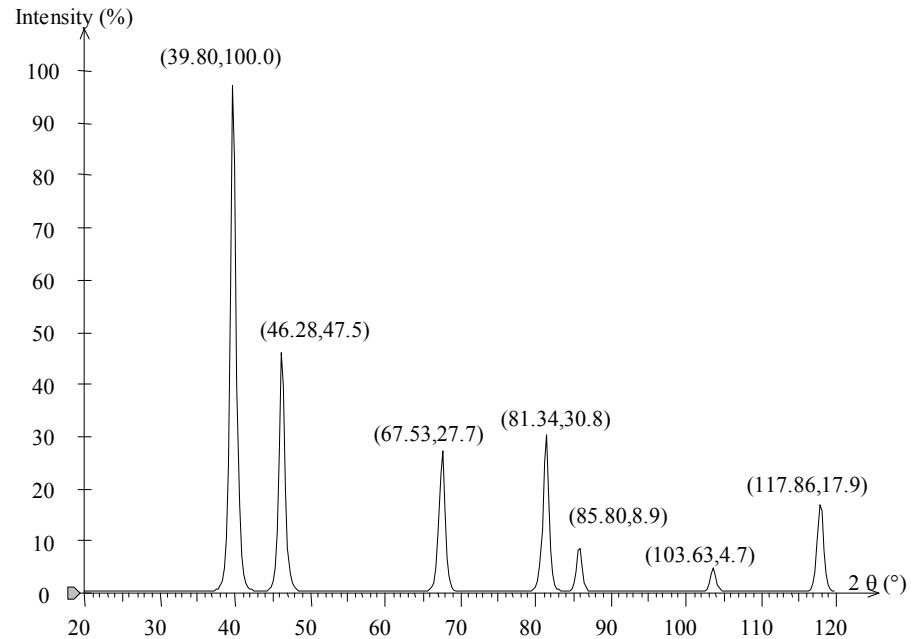
2 θ	Intensity (%)	d (Å)
39.80	100.00	2.263
46.28	47.50	1.960
67.53	27.70	1.385
81.34	30.80	1.182
85.80	8.90	1.132
103.63	4.70	0.980
117.86	17.90	0.899



Continued

2. Identify the 3 most intense peaks and label them.

- Most intense: d_1 ;
- Second most intense: d_2 ;
- Third most intense: d_3 .



3. Locate proper d_1 group in the Hanawalt (numerical) Search Manual

Group 2.29-2.23 (± 0.01) \rightarrow

2θ	Intensity (%)	d
<i>39.80</i>	<i>100.00</i>	<i>2.263</i>
<i>46.28</i>	<i>47.50</i>	<i>1.960</i>
67.53	27.70	1.385
<i>81.34</i>	<i>30.80</i>	<i>1.182</i>
85.80	8.90	1.132
103.63	4.70	0.980
117.86	17.90	0.899



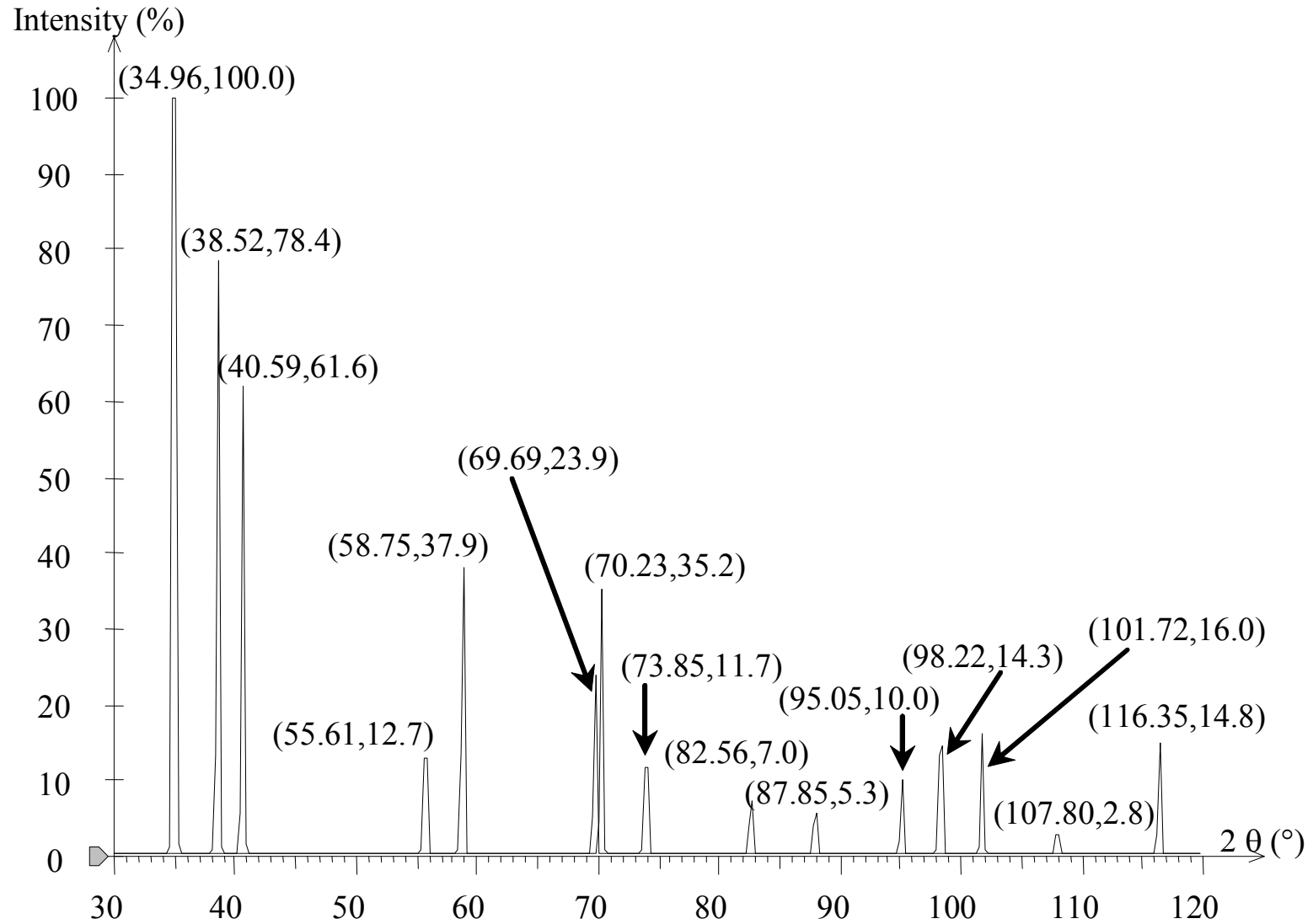
Continued

4. Match d_1 ; look for match to d_2 and then repeat for d_3 .
5. Once all three match, compare relative intensities with tabulated values.
6. When the experimental d -spacings and intensities for the most intense reflections match those in the Hanawalt manual, get the ICDD card and compare for all reflections. Once all agree, you will have matched the pattern and identified the unknown.

Additional Notes

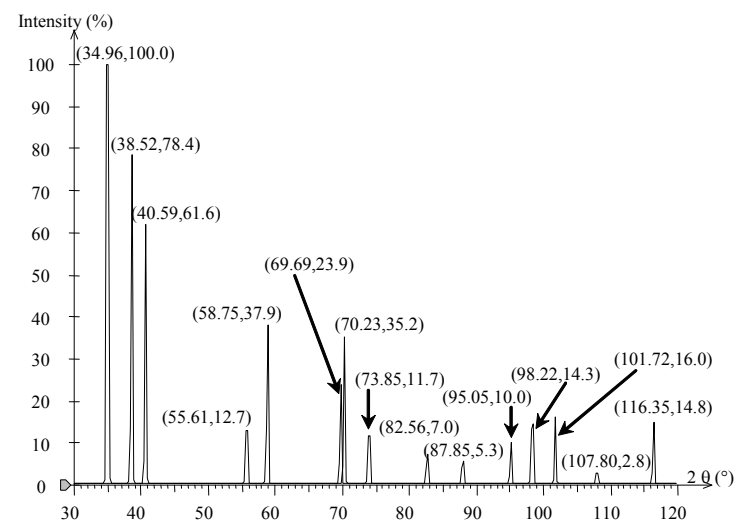
- This method of analysis will work for multiphase materials, no matter how many phases are present.
- The technique is the basic one that most computer phase ID programs use.
- Works for powders. Some difficulties arise with bulk materials.

Multiphase Unknowns



Multiphase Unknown – cont'd

2theta	Intensity (cps)	I/I ₀	d (Å)
34.96	89558.4	100.0	2.57
38.52	70211.3	78.4	2.34
40.59	55128.3	61.6	2.22
55.61	11353.3	12.7	1.65
58.75	33939.3	37.9	1.57
69.69	21387.7	23.9	1.35
70.23	31522.6	35.2	1.34
73.85	10494.4	11.7	1.28
82.56	6292.7	7.0	1.17
87.85	4734.2	5.3	1.11
95.05	8962.5	10.0	1.04
98.22	12845.8	14.3	1.02
101.72	14293.5	16.0	0.99
107.80	2534.4	2.8	0.95
116.35	13242.4	14.8	0.91



Three strongest peaks:

- $d_1 = 2.57 \text{ \AA}$ $I/I_0 = 100$
- $d_2 = 2.34 \text{ \AA}$ $I/I_0 = \sim 80$
- $d_3 = 2.22 \text{ \AA}$ $I/I_0 = \sim 60$

The Process



Use 2.57 – 2.51 (± 0.01) group in search manual

Excerpt from Search Manual (1993 edition, p. 1003)

	Strongest reflections								Formula	PDF #
o	2.58 ₈	2.33 _x	2.55 ₈	1.55 _x	1.44 ₉	1.40 ₉	1.38 ₉	1.27 ₇	CoZr ₄	23- 945
	2.57 ₅	2.33 ₅	2.18 ₅	1.15 _x	1.16 ₅	3.28 ₄	2.91 ₄	1.67 ₄	CeCr ₂ B ₆	26- 350
→	2.56 _x	2.33 ₆	2.08 ₆	1.25 ₆	1.16 ₆	2.70 ₅	1.54 ₅	1.45 ₅	ThTc ₂	18-1319
→	2.56 _x	2.33 ₈	2.07 ₈	1.19 ₈	1.34 ₆	0.89 ₆	0.86 ₃	1.40 ₂	GeHf ₂	15- 728
	2.55 ₈	2.33 _x	2.58 ₅	1.55 _x	1.44 ₉	1.40 ₉	1.38 ₉	1.27 ₇	CoZr ₄	23- 945

Note only two possible matches based on our identified d_1 and d_2 :

- ThTc₂
 - GeHf₂
- (on basis of peak intensity and d-spacing)

However, neither of these has 2.22 as the third most intense reflection. In addition, the intensity of our second most intense peak does not match with the patterns for ThTc₂ or GeHf₂ (from subscripts in search manual).

Thus, it is likely that our second and/or third reflections belong to another phase.

The Process – cont'd



Let's search again treating the third most intense peak as d_2 and our fourth most intense peak as d_3 .

- $d_1 = 2.57 \text{ \AA}$ $I/I_0 = 100$
- $d_2 = 2.22 \text{ \AA}$ $I/I_0 = \sim 80$
- $d_3 = 1.57 \text{ \AA}$ $I/I_0 = \sim 40$

Use the 2.57 – 2.51 (± 0.01) group in search manual

Excerpt from Search Manual (1993 edition, p. 1004)

	Strongest reflections								Formula	PDF #
o	2.57 _x	2.23 ₂	1.57 ₂	1.57 ₂	2.20 ₁	1.58 ₁	1.33 ₁	1.29 ₁	TiH _{1.924}	25- 983
→ *	2.57 _x	2.23 ₇	1.58 ₄	1.34 ₄	1.29 ₁	1.00 ₁	1.02 ₁	1.11 ₁	TaC	← 35- 801
o	2.56 ₈	2.23 _x	2.45 ₈	2.36 ₈	2.20 ₈	2.09 ₈	3.18 ₆	2.43 ₆	Pd _{2.5} Se	11- 499
i	2.52 _x	2.23 _x	2.22 _x	2.21 _x	2.98 ₈	2.97 ₈	6.66 ₅	3.31 ₅	Cu ₁₅ Hg ₁₁	15- 728
	2.52 _x	2.23 _x	2.15 _x	2.11 _x	4.54 ₈	3.63 ₈	3.94 ₆	2.32 ₆	β -Ga ₃ Re	36-1103

- ➡ On the basis of our new d_1 , d_2 , and d_3 and their relative intensities (taking into account the $\pm 0.01 \text{ \AA}$ error in the tables), the only possible match appears to be TaC.
- ➡ The only other phase that is close is TiH_{1.924}, however its peak intensities do not match the experimental pattern.
- ➡ Compare with ICDD/JCPDS Card

ICDD card for TaC

35-0801

Wavelength= 1.54056

*

TaC

d(A) Int h k l

Tantalum Carbide

2.5718 100 1 1 1

2.2276 70 2 0 0

1.5749 41 2 2 0

Tantalcarbide, syn

1.3428 41 3 1 1

1.2857 14 2 2 2

Rad.: CuK α 1 λ : 1.540598 Filter: Graph Mono d-sp: Diff.

1.1139 6 4 0 0

Cut off: Int.: Diffract. I/Icor.:

1.0218 10 3 3 1

Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 21, 124 (1984)

.9960 12 4 2 0

.9094 3 4 2 2

.8573 5 5 1 1

Sys.: Cubic

S.G.:Fm3m (225)

a: 4.4547(2) b: c: A: C:

α : β : γ : Z: 4 mp:

Ref: Ibid.

Dx: 14.498 Dm: SS/FOM: $\bar{1}0 = 9\epsilon(.0102, 10)$

Color: Dark brownish gray

Peak height intensity. The mean temperature of data collection was 24.0 C. The sample was obtained from Aesar Division of Johnson Matthey, Inc., Seabrook, New Hampshire, USA. CAS #: 12070-06-3. $\sigma(I_{obs}) = \pm 0.01$. Cl Na type. Halite group, periclase subgroup. Silver used as an internal stand. PSC: cF8. To replace 19-1292. Mwt: 192.96. Volume[CD]: 88.40.

FROM EXPERIMENT

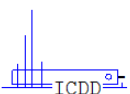
• $d_1 = 2.57 \text{ \AA}$ $I/I_0 = 100$

• $d_2 = 2.22 \text{ \AA}$ $I/I_0 = \sim 80$

• $d_3 = 1.57 \text{ \AA}$ $I/I_0 = \sim 40$

• $d_4 = 1.34 \text{ \AA}$ $I/I_0 = \sim 40$

Etc...



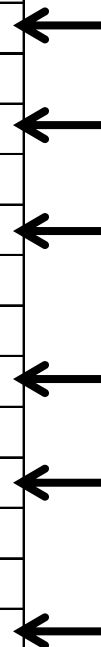
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ID of unknown #1 in the multiphase pattern



Observed					ICDD/JCPDS Card 35-801		
2theta	intensity	I/I _o (%)	d _{hkl}	hkl	Phase	d _{hkl}	I/I _o (%)
34.96	89558.4	100	2.57	(1 1 1)	TaC	2.572	100
38.52	70211.3	78	2.34				
40.59	55128.3	62	2.22	(2 0 0)	TaC	2.228	70
55.61	11353.3	13	1.65				
58.75	33939.3	38	1.57	(2 2 0)	TaC	1.575	41
69.69	21387.7	24	1.35				
70.23	31522.6	35	1.34	(3 1 1)	TaC	1.343	41
73.85	10494.4	12	1.28	(2 2 2)	TaC	1.286	14
82.56	6292.7	7	1.17				
87.85	4734.2	5	1.11	(4 0 0)	TaC	1.114	6
95.05	8962.5	10	1.04				
98.22	12845.8	14	1.02	(3 3 1)	TaC	1.023	10
101.72	14293.5	16	0.99	(4 2 0)	TaC	0.996	12
107.8	2534.4	3	0.95				
116.35	13242.4	15	0.91	(4 2 2)	TaC	0.909	3



ID of unknown #2 in the multiphase pattern

Take second set of peaks and normalize intensities with respect to the remaining unidentified peaks.

Observed				
2theta	Intensity	I/I _o (%)	<i>d</i> _{hkl}	<i>hkl</i>
38.52	70211.3	100	2.34	
55.61	11353.3	16	1.65	
69.69	21387.7	30	1.35	
82.56	6292.7	9	1.17	
95.05	8962.5	13	1.04	
107.8	2534.4	4	0.95	

Let's search again treating the most intense peak as d_1 , the second as d_2 , and the third as d_3 .

- $d_1 = 2.34 \text{ \AA}$ $I/I_0 = 100$
- $d_2 = 1.35 \text{ \AA}$ $I/I_0 = \sim 30$
- $d_3 = 1.65 \text{ \AA}$ $I/I_0 = \sim 20$

ID of unknown #2 in the multiphase pattern – cont'd

Use 2.36 – 2.30 (± 0.01) group in search manual

Excerpt from Search Manual (1993 edition, p. 1078)

	Strongest reflections								Formula	PDF #
*	2.34_x	1.35₄	1.65₂	0.88₃	1.05₂	1.17₁	0.95₁	0.83₁	Ta	4- 788
	2.33_x	1.35₈	1.99₅	1.65 ₅	3.81 ₂	1.52 ₂	1.27 ₂	3.30 ₁	Ag ₂ LiSn	23- 639
i	2.33_x	1.35₅	1.65₂	1.17 ₁	0.00 ₁	0.00 ₁	0.00 ₁	0.00 ₁	Ta _{0.5} V _{0.5} D	39-1334
	2.33_x	1.35_x	1.17_x	1.65 ₈	3.24 ₅	2.08 ₅	1.29 ₅	1.20 ₅	α' -NbN	43-1420
	2.29_x	1.35₄	2.43₃	1.37 ₂	0.90 ₂	2.88 ₂	1.06 ₂	1.86 ₁	Ta ₂ B	25- 920

On the basis of our new d_1 , d_2 , and d_3 , their relative intensities, and taking into account the ± 0.01 Å error in the tables, the only possible match appears to be Ta (card # 4-0788).

Compare with ICDD/JCPDS Card

ICDD card for Ta

04-0788

Wavelength= 1.54056

*

Ta	d(A)	Int	h	k	l
Tantalum	2.338	100	1	1	0
	1.653	21	2	0	0
	1.35	38	2	1	1
	1.1687	13	2	2	0
	1.0453	19	3	1	0
	.9543	7	2	2	2
	.8835	29	3	2	1
	.8265	4	4	0	0

Rad.: CuK α 1 λ : 1.5405 Filter: Ni Beta d-sp:
 Cut off: Int.: Diffract. I/Icor.: 4.44
 Ref: Swanson, Tatge, Natl. Bur. Stand. (U.S.), Circ. 539, I, 29 (1953)

Sys.: Cubic S.G.:Im3m (229)
 a: 3.3058 b: c: A: C:
 α : β : γ : Z: 2 mp:
 Ref: Ibid.

Dx: 16.634 Dm: SS/FOM: $\bar{g} = 10^4 (.0092, 8)$

Color: Gray
 Pattern taken at 26 C. Sample procured from Johnson Matthey Company, Ltd., London, England, UK. CAS #: 7440-25-7. The material contained dissolved gases which caused broadening of diffraction peaks, and TaH, which contributed extra reflections. After annealing at 1500 C in vacuum for 30 minutes in a tantalum boat, the sample gave very sharp reflections including only traces of the hydride. Spectroscopic analysis shows faint traces of Nb, Al, Si, Fe, Mn. Color from Merck Index, 8th Ed., p. 1012. W type. PSC: cI2. Mwt: 180.95. Volume[CD]: 36.13.

FROM EXPERIMENT

- $d_1 = 2.34 \text{ \AA}$ $I/I_0 = 100$
- $d_2 = 1.65 \text{ \AA}$ $I/I_0 = \sim 30$
- $d_3 = 1.35 \text{ \AA}$ $I/I_0 = \sim 20$
- $d_4 = 1.17 \text{ \AA}$ $I/I_0 = \sim 10$

Etc...



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ID of unknown #2 in the multiphase pattern

Identification of second unknown in multiphase material

Observed					ICDD/JCPDS Card 4- 788		
2theta	intensity	I/I _o (%)	d _{hkl} (Å)	hkl	Phase	d _{hkl} (Å)	I/I _o (%)
38.52	70211.3	100	2.34	(1 1 0)	Ta	2.338	100
55.61	11353.3	16	1.65	(2 0 0)	Ta	1.653	21
69.69	21387.7	30	1.35	(2 1 1)	Ta	1.350	38
82.56	6292.7	9	1.17	(2 2 0)	Ta	1.1687	13
95.05	8962.5	13	1.04	(3 1 0)	Ta	1.0453	19
107.8	2534.4	4	0.95	(2 2 2)	Ta	0.9543	7

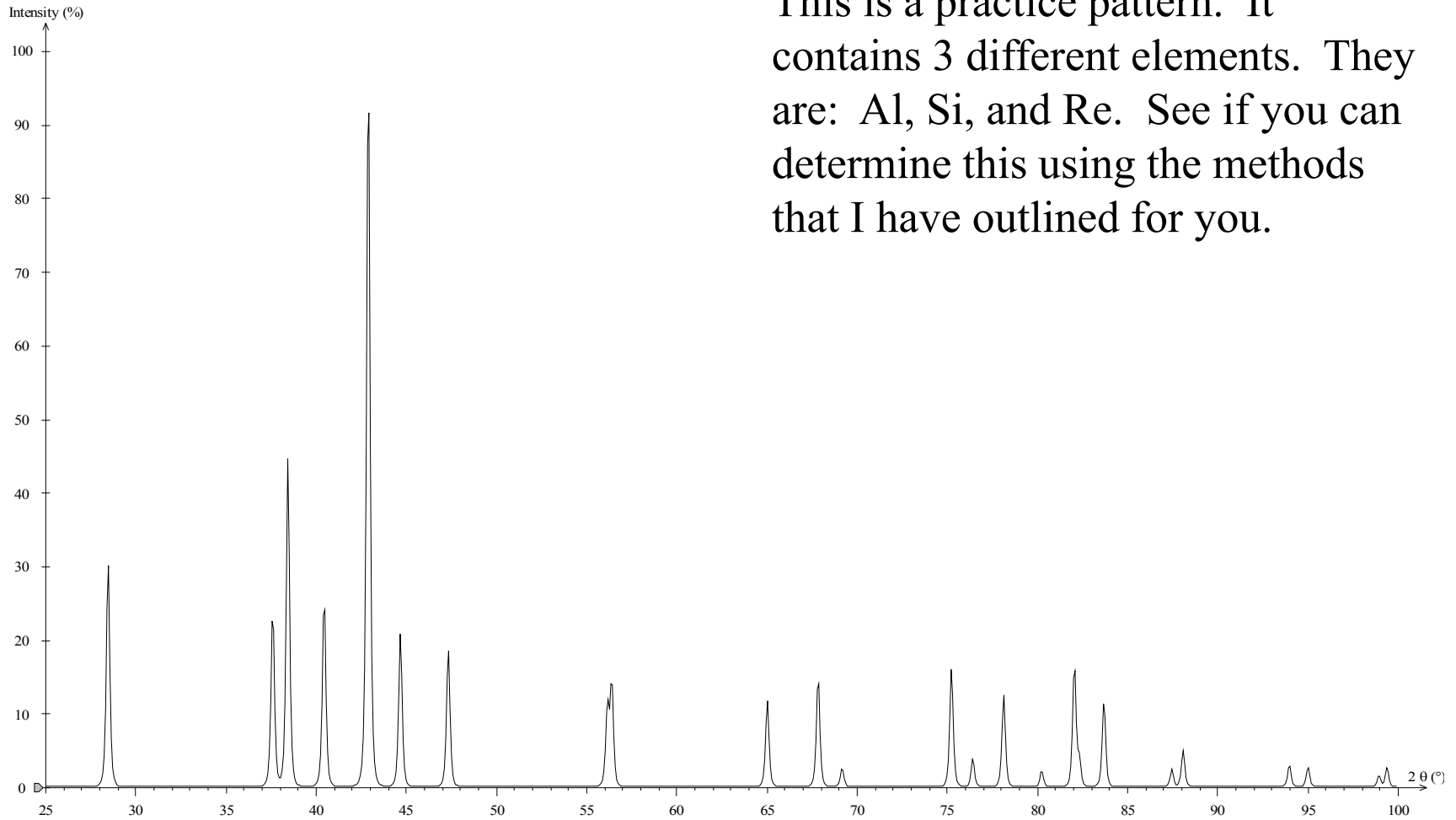
“This unknown is composed of Ta and TaC!”

Applicability of the Method

- This method works for any combination or number of phases.
- It can be very tedious!

Other techniques that could be useful

- Light optical microscopy, scanning electron microscopy, x-ray spectroscopy, mass spectroscopy, wet chemical analysis, etc...
- These techniques may allow us to:
 - Determine number of phases present in the unknown
 - Determine elements that are present in the unknown
 - Etc...
- They can provide supplementary information
- You will do this in your final group projects.



This is a practice pattern. It contains 3 different elements. They are: Al, Si, and Re. See if you can determine this using the methods that I have outlined for you.

Here is the relevant XRD data for the pattern. I strongly suggest that you try it.

2theta	intensity	d _{hkl}		2theta	intensity	d _{hkl}
28.45	1532.9	3.134		82.04	832.8	1.174
37.59	1215.7	2.391		82.33	174.0	1.17
38.43	2220.8	2.341		83.68	590.9	1.155
40.44	1312.6	2.229		87.45	117.0	1.114
42.89	4964.8	2.107		88.08	248.5	1.108
44.67	1042.2	2.027		93.97	149.4	1.054
47.32	945.1	1.919		95.00	34.6	1.045
56.15	534.6	1.637		98.93	80.3	1.013
56.39	699.8	1.63		99.39	135.7	1.01
65.02	585.8	1.433		106.77	86.1	0.96
67.83	757.1	1.38		111.58	367.4	0.931
69.16	131.5	1.357		111.83	270.6	0.93
75.23	811.0	1.262		114.16	164.1	0.918
76.41	189.2	1.245		116.36	264.5	0.907
78.13	618.9	1.222		116.94	122.3	0.904
80.23	111.1	1.196				