Analytical Methods for Materials

Laboratory Module #8

Identification of Unknowns via X-ray Diffraction Techniques

Suggested Reading

- **Y. Waseda, E. Matsubara, K. Shinoda, *X-ray Diffraction Crystallography*, (Springer, New York, 2011), pages 117-119, 139-144.**
- C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 237-249.
- B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, (Prentice-Hall, Upper Saddle River, NJ, 2001), Ch. 9, pages 275-294.

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.

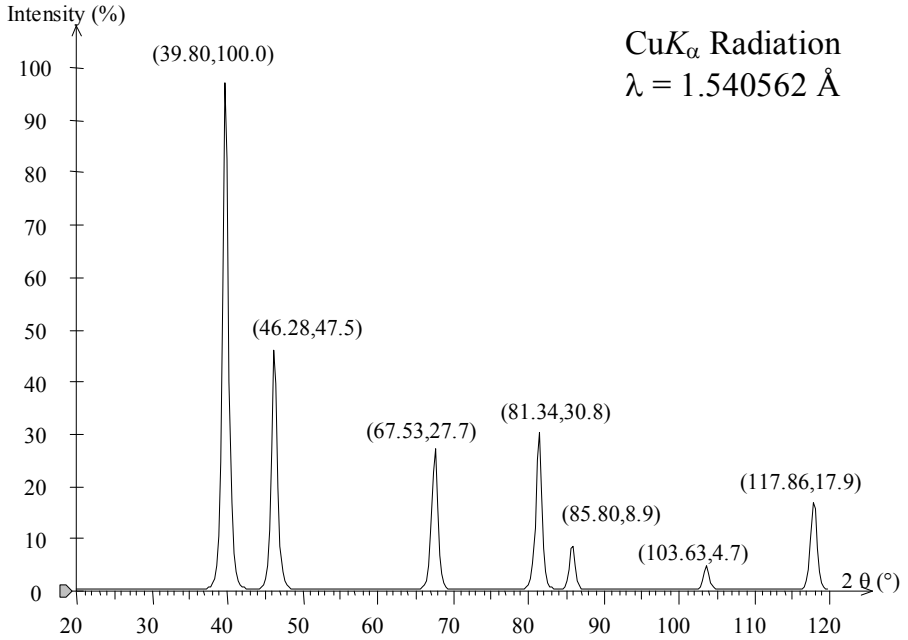
Introduction

- 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.

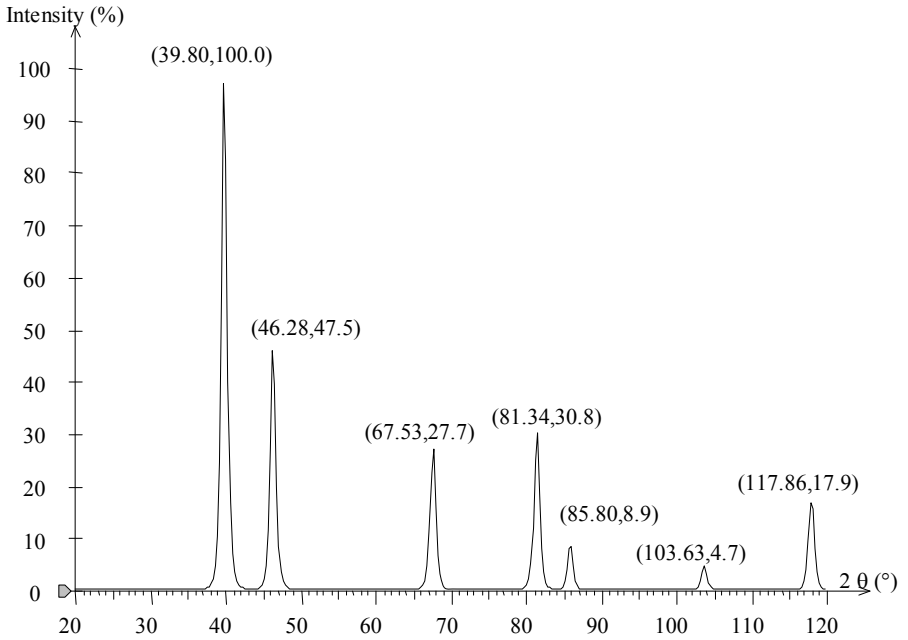


$$n\lambda = 2d\sin\theta$$

2θ	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 (±.01)

2θ	Intensity (%)	d
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

4. Match d_1; look for match to d_2 and then repeat for d_3.

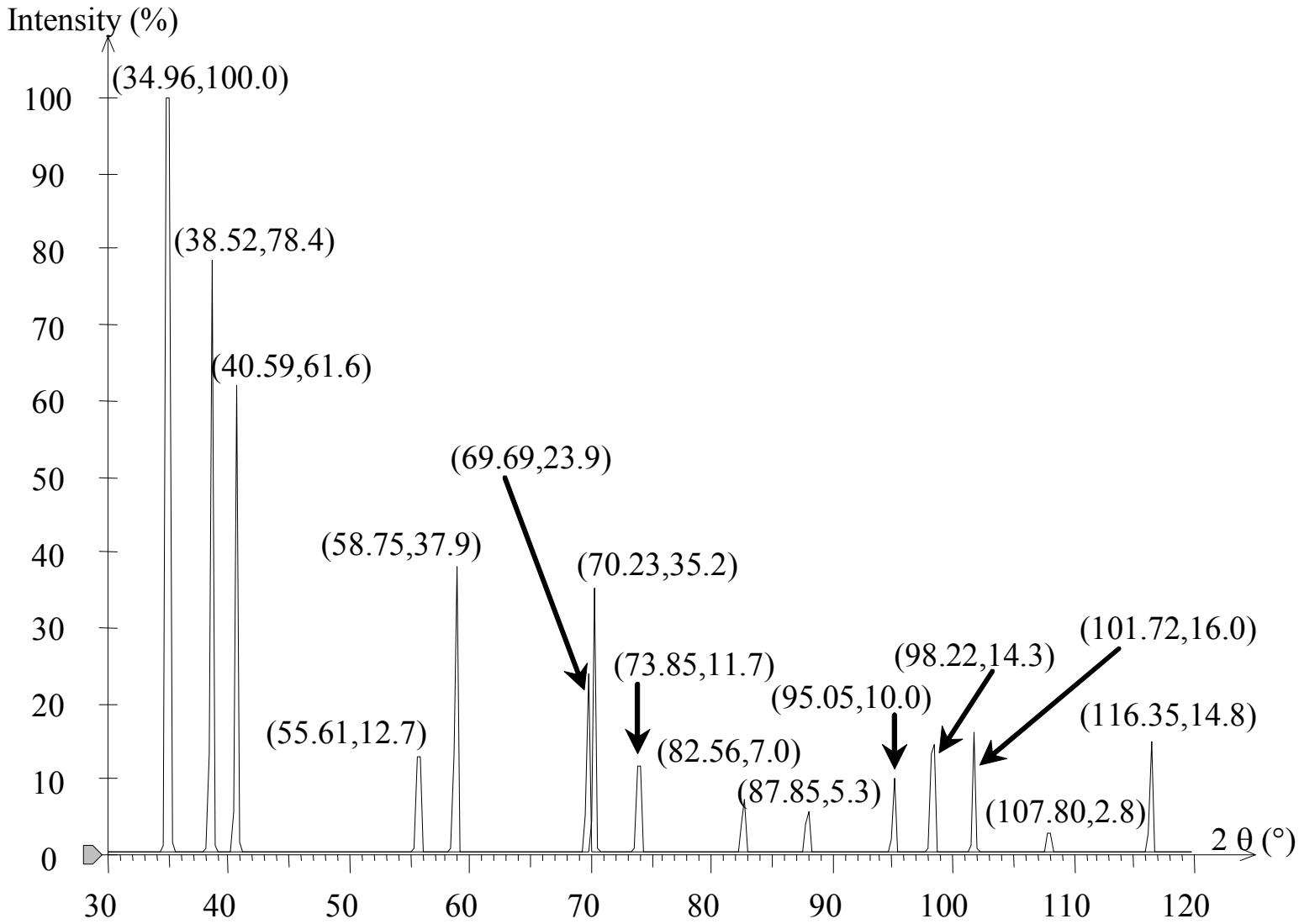
5. Once all three match, compare relative intensities with tabulated values.

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

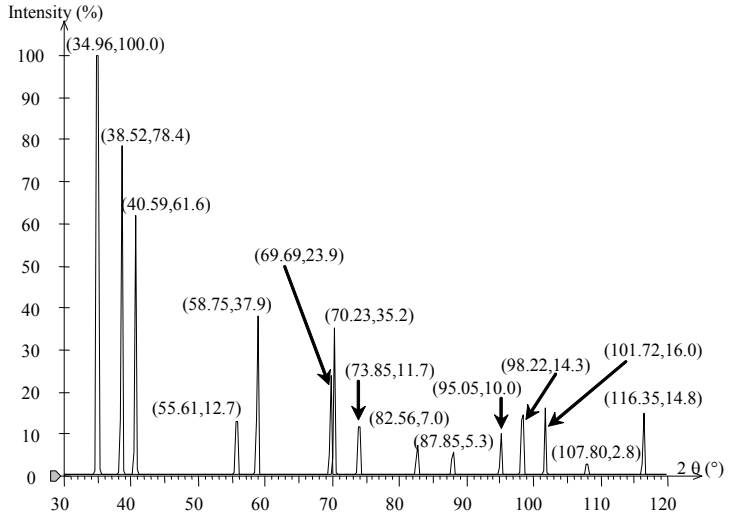
- This method of analysis will work for multiphase materials, no matter how many phases are present.
- The technique is the basic one that most computer phase ID programs use.
- Works for powders. Some difficulties arise with bulk materials.

Multiphase Unknowns



Multiphase Unknown – cont'd

2theta	Intensity (cps)	I/I_o	*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:

- $d_1 = 2.57$ Å $I/I_o = 100$
- $d_2 = 2.34$ Å $I/I_o = \sim 80$
- $d_3 = 2.22$ Å $I/I_o = \sim 60$

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$_4$	$CeCr_2B_6$	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:

- $ThTc_2$
- $GeHf_2$

(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 $ThTc_2$ or $GeHf_2$ (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 Å I/I_o = 100
- d_2 = 2.22 Å I/I_o = ~80
- d_3 = 1.57 Å I/I_o = ~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	**2.57x**	**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
*	**2.57x**	**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$_8$**	**2.23x**	**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	**2.52x**	**2.23x**	**2.22x**	2.21x	2.98$_8$	2.97$_8$	6.66$_5$	3.31$_5$	$Cu_{15}Hg_{11}$	15- 728
	2.52x	**2.23x**	**2.15x**	2.11x	4.54$_8$	3.63$_8$	3.94$_6$	2.32$_6$	β-Ga_3Re	36-1103

- On the basis of our new d_1, d_2, and d_3 and their relative intensities (taking into account the ±0.01 Å 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

Tantalum Carbide

Tantalcarbide, syn

Rad.: CuKa1 λ: 1.540598 Filter: Graph Mono d-sp: Diff.

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

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

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: $\bar{1}0$ = 9ε(.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. σ(I obs)= ±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.

d(A)	Int	h	k	l
2.5718	100	1	1	1
2.2276	70	2	0	0
1.5749	41	2	2	0
1.3428	41	3	1	1
1.2857	14	2	2	2
1.1139	6	4	0	0
1.0218	10	3	3	1
.9960	12	4	2	0
.9094	3	4	2	2
.8573	5	5	1	1

FROM EXPERIMENT

- d_1 = 2.57 Å I/I_o = 100
- d_2 = 2.22 Å I/I_o = ~80
- d_3 = 1.57 Å I/I_o = ~40
- d_4 = 1.34 Å I/I_o = ~40

Etc…

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 (%)	d_{hkl}	*hkl*
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.

- $d_1 = 2.34$ Å $I/I_o = 100$
- $d_2 = 1.35$ Å $I/I_o = \sim 30$
- $d_3 = 1.65$ Å $I/I_o = \sim 20$

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$_X$**	**1.35$_4$**	**1.65$_2$**	0.88$_3$	1.05$_2$	1.17$_1$	0.95$_1$	0.83$_1$	Ta	4- 788
	2.33$_X$	**1.35$_8$**	**1.99$_5$**	1.65$_5$	3.81$_2$	1.52$_2$	1.27$_2$	3.30$_1$	Ag_2LiSn	23- 639
i	**2.33$_X$**	**1.35$_5$**	**1.65$_2$**	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$_X$	**1.35$_4$**	**2.43$_3$**	1.37$_2$	0.90$_2$	2.88$_2$	1.06$_2$	1.86$_1$	Ta_2B	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

Tantalum

Rad.: CuKa1 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: $\bar{8}$ = 10(.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.

d(A)	Int	h	k	l
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

FROM EXPERIMENT

- d_1 = 2.34 Å I/I_o = 100
- d_2 = 1.65 Å I/I_o = ~30
- d_3 = 1.35 Å I/I_o = ~20
- d_4 = 1.17 Å I/I_o = ~10

Etc…

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!"

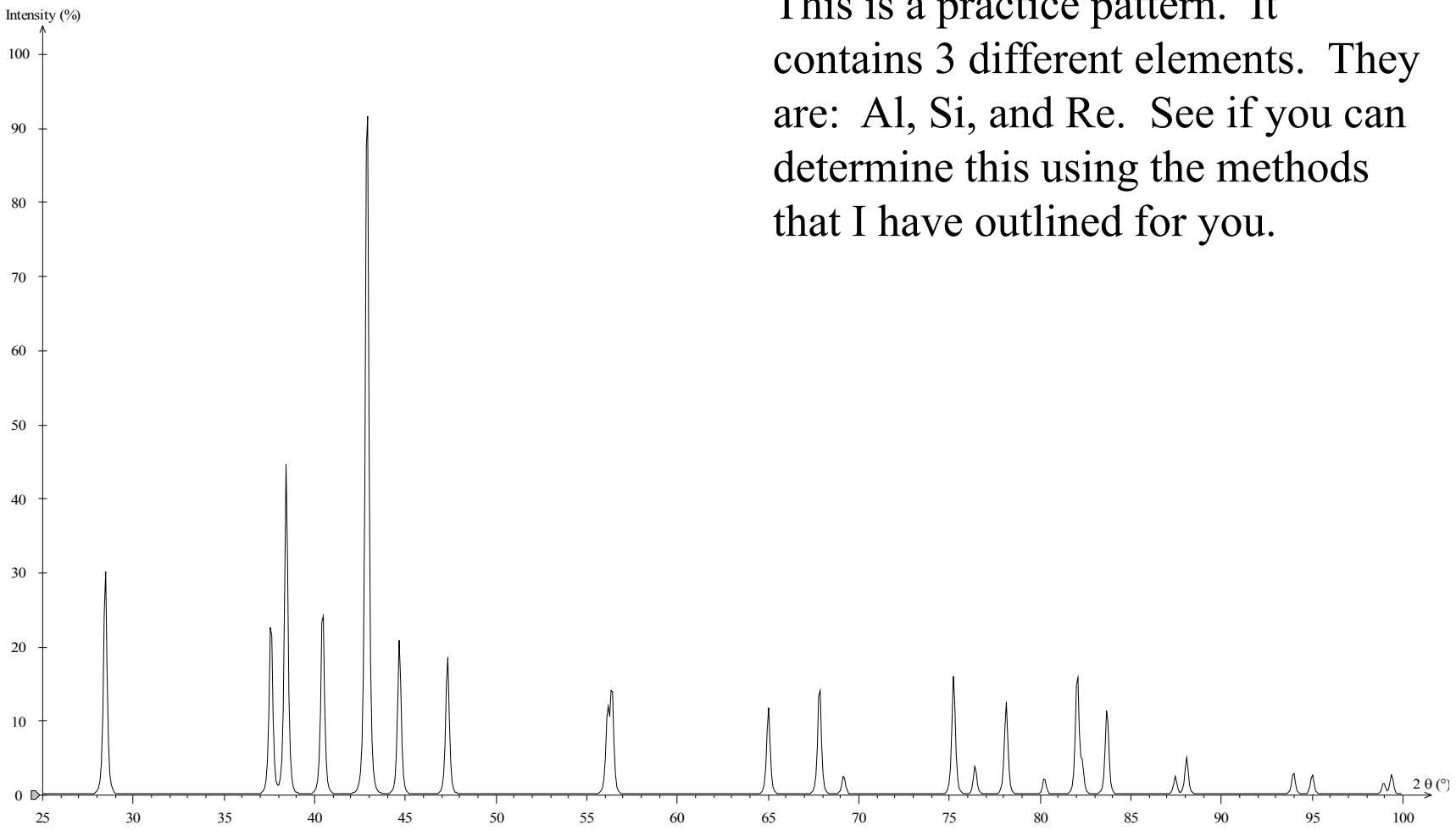
Applicability of the Method

- 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				