

PPXRD ROUND ROBIN

-

RESULTS ANALYSIS AND  
CLUSTER ANALYSIS



# Many Thanks

- Bruker-AXS PolySnap
- PANalytical – X’Pert HighScore Plus (Cluster Analysis)

Gordon Barr  
Thomas Degan  
Thomas Dortmann  
Martijn Fransen  
Chris Gilmore  
Arnt Kern

# METHOD

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- Tested cluster analysis programs by using data from SRM 1976 alumina plate from ICDD grantees  
*(prepared plate – eliminates specimen preparation variables, tests instrument calibrations and resolution)*
- Input and analyzed data sets from PPXRD round robin

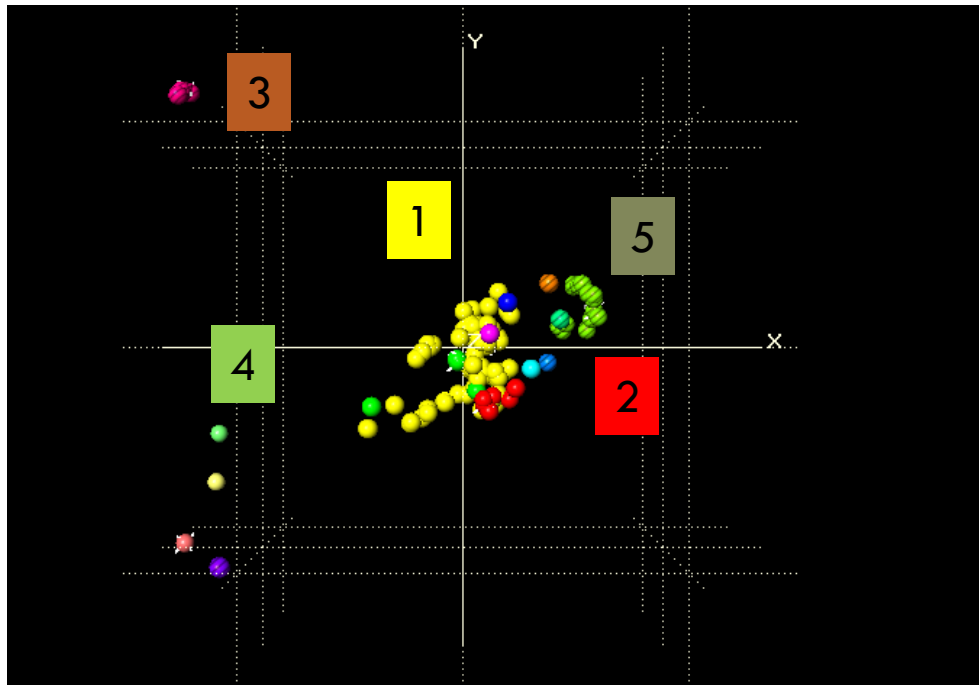
# Program Tests

## - SRM 1976

- 102 Data Sets
- Collected by ICDD grantees as proof of instrument calibration required with the submission of reference materials

# SRM 1976 – 102 Datasets

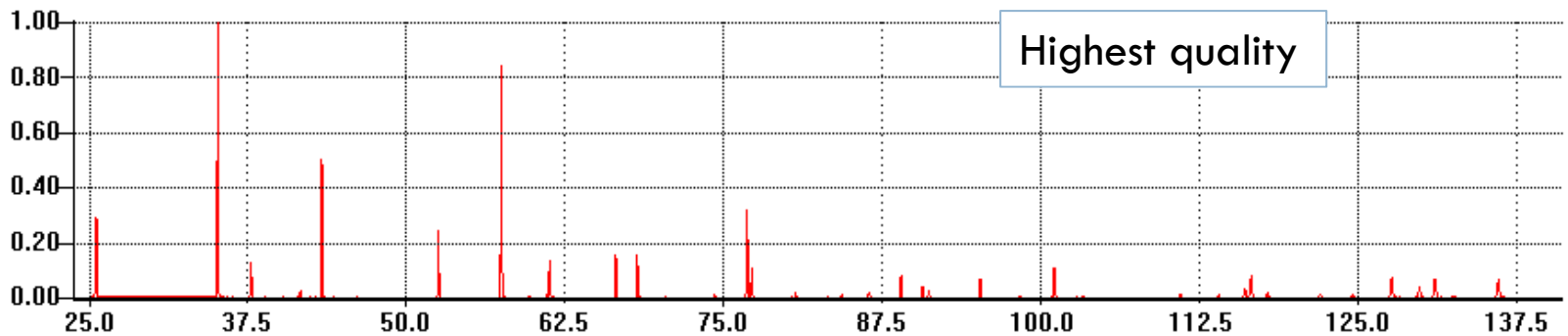
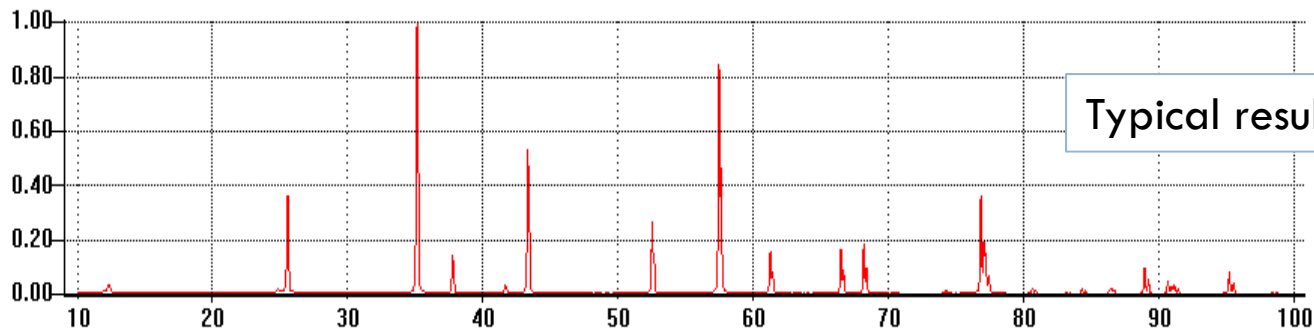
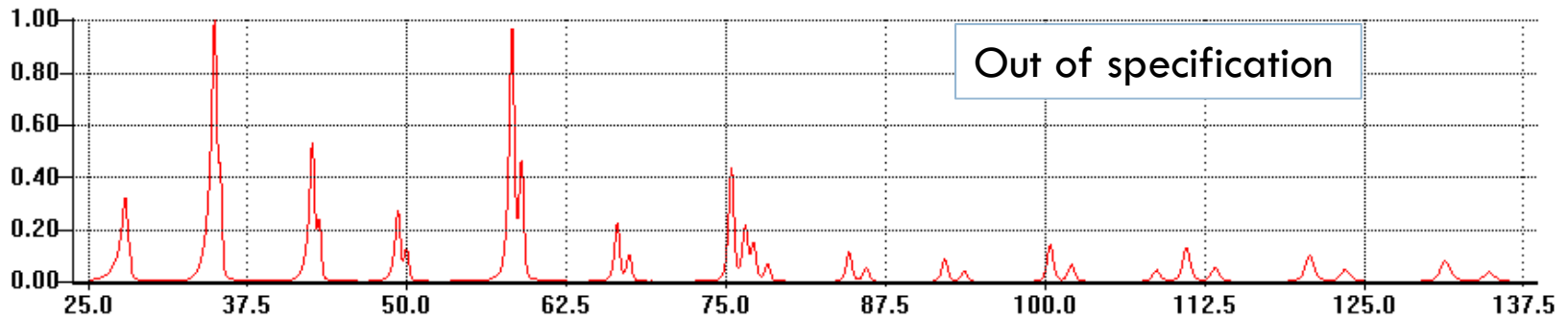
## PolySnap – MMDS Plot



- 1) Typical data set of corundum plate
- 2) Highest resolution – alpha one only
- 3) Poor resolution data – out of specification
- 4) Not clustered – mislabeled sample (not corundum), other samples with bad scatter interferences
- 5) Resolution optimized diffractometer with alpha one/alpha two doublets

2 and 5 are highest quality – and are produced by very experienced well known grantees

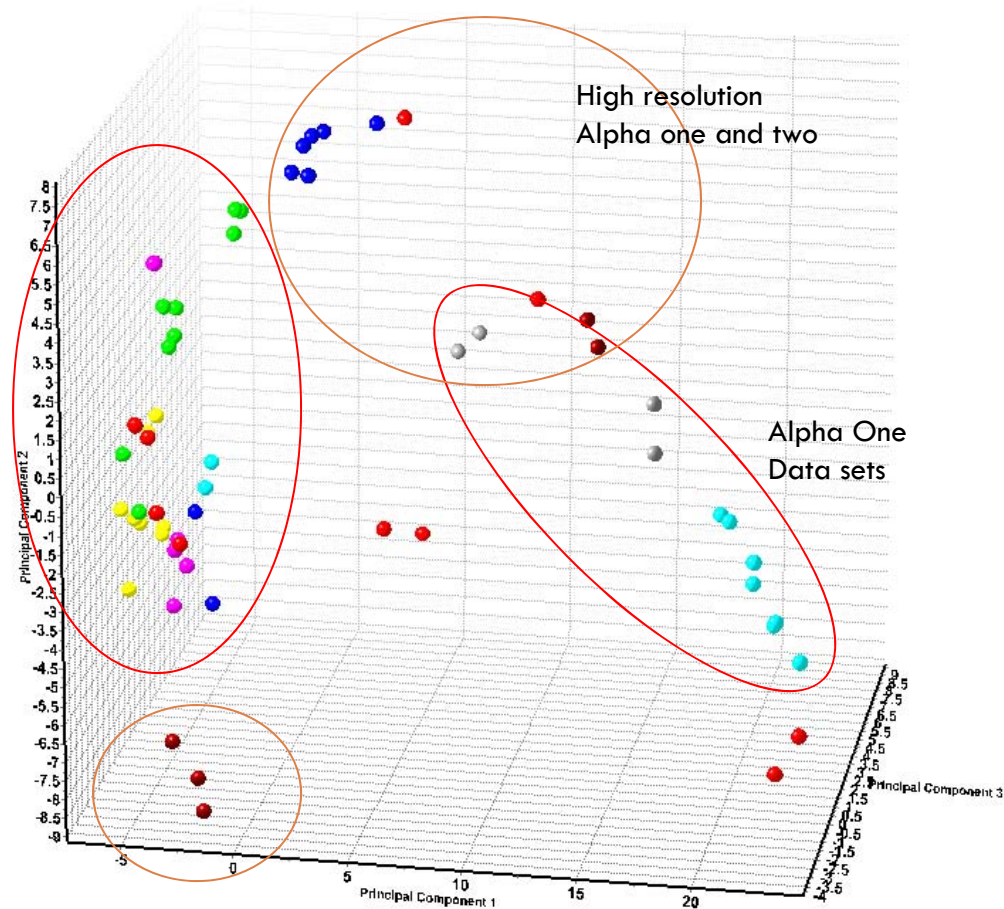
# Cluster Examples



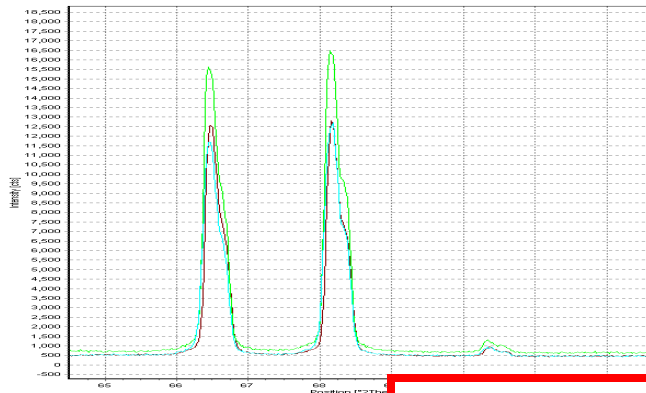
# SRM 1976 – 102 Datasets

## HighScore Plus Cluster – PCM Plot

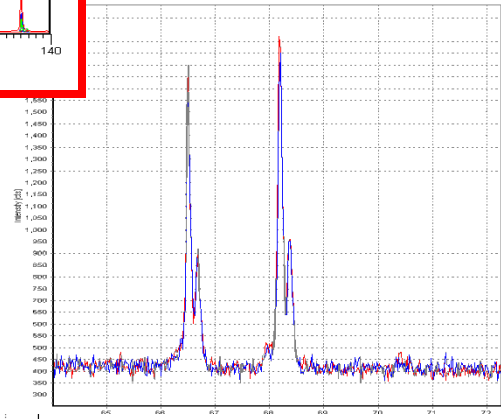
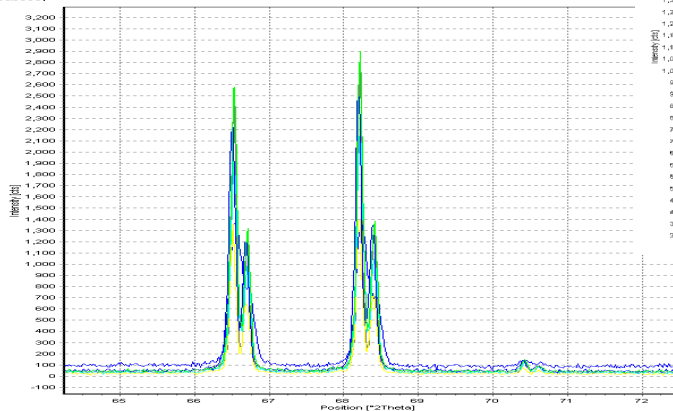
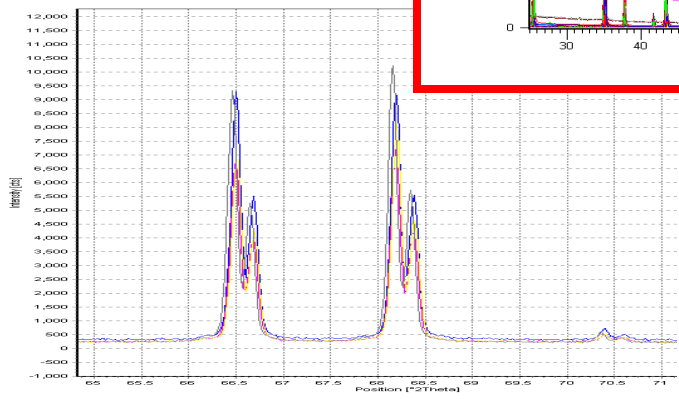
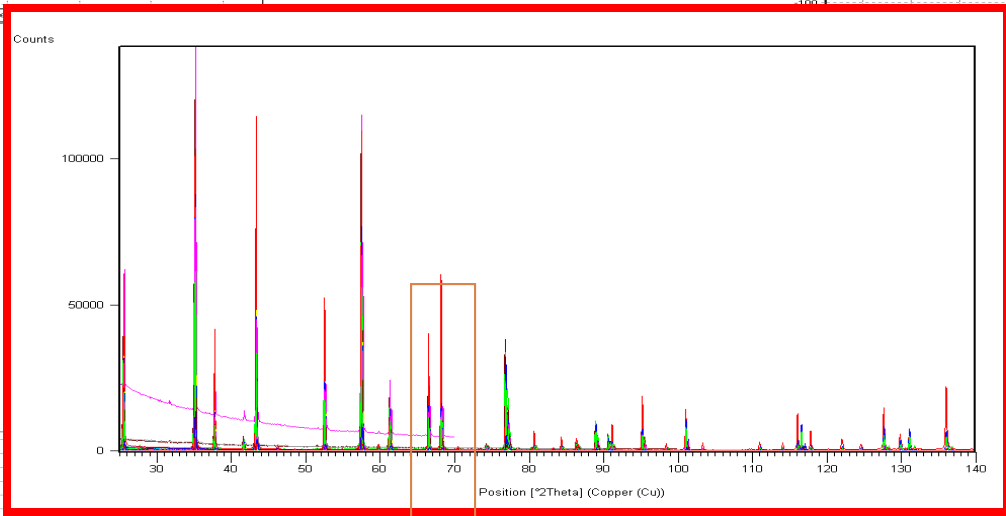
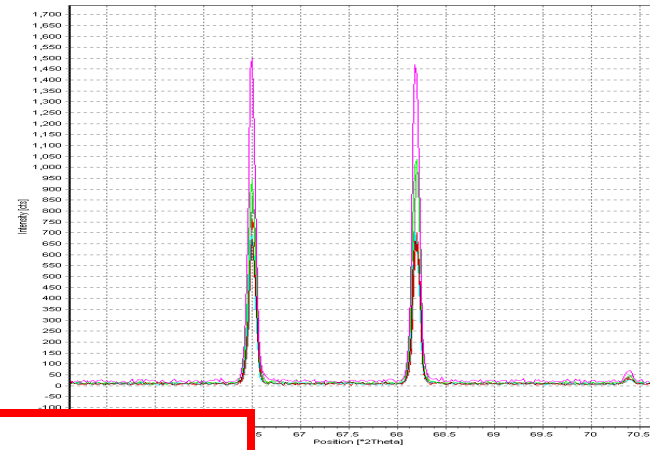
Yellow, 10 to 100 degrees  
Red, 10 to 120 degrees  
Green, 10 to 140 degrees



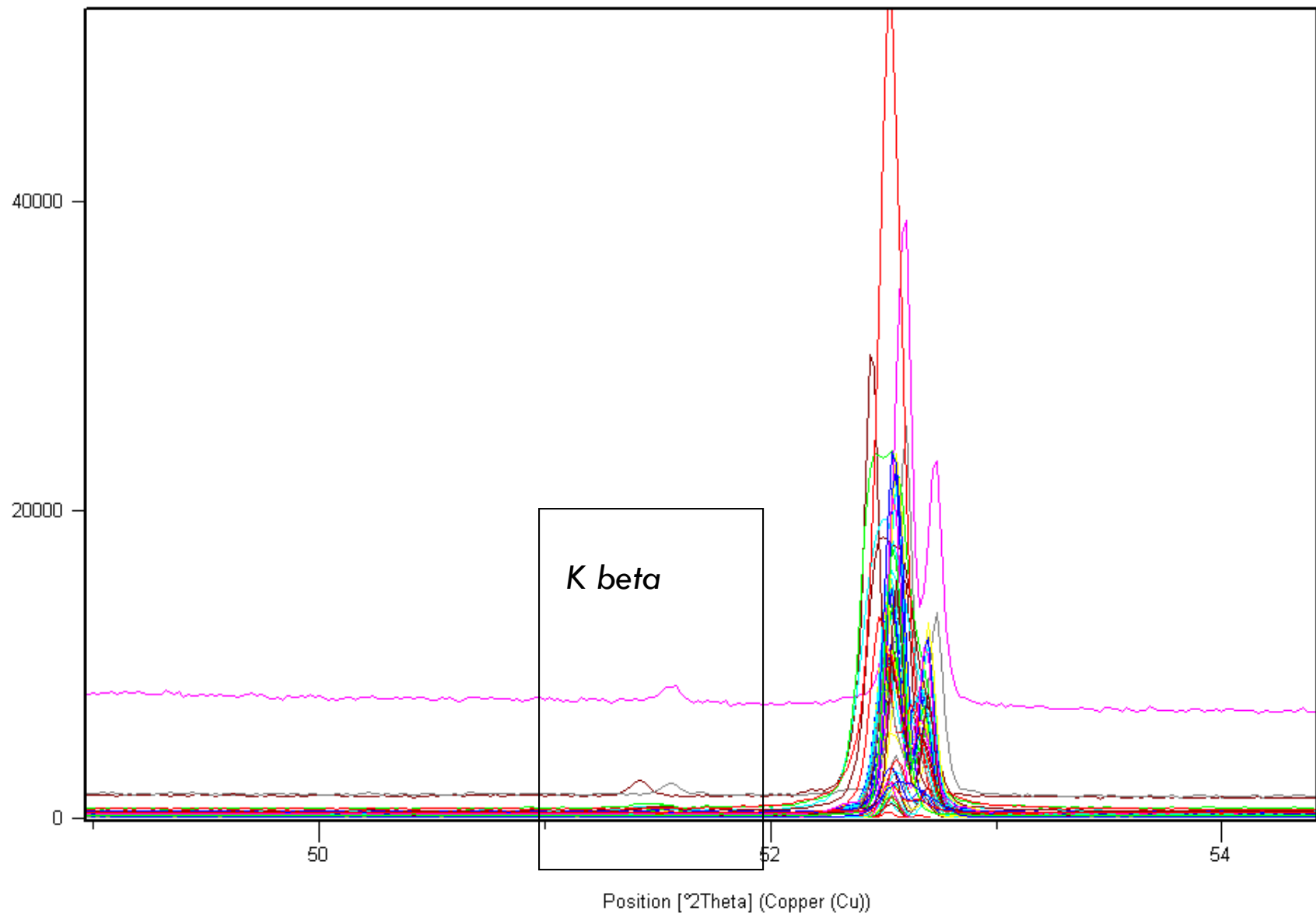
Low resolution  
cluster



Various Profile Resolutions



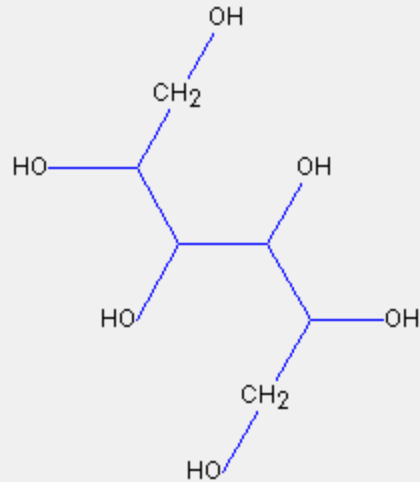
Counts



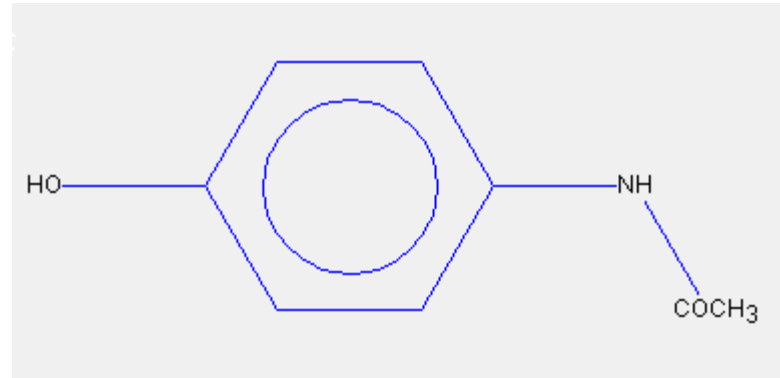
# PPXRD Round Robin

- 16 Sample sets distributed
- 11 Laboratories supplied results, 9 with raw data
- 3 Samples were in each set
- 1 g samples, vortex mixed
- 63 Data sets have been analyzed

# Round Robin Specimens



**Beta D-Mannitol**  
**C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>**



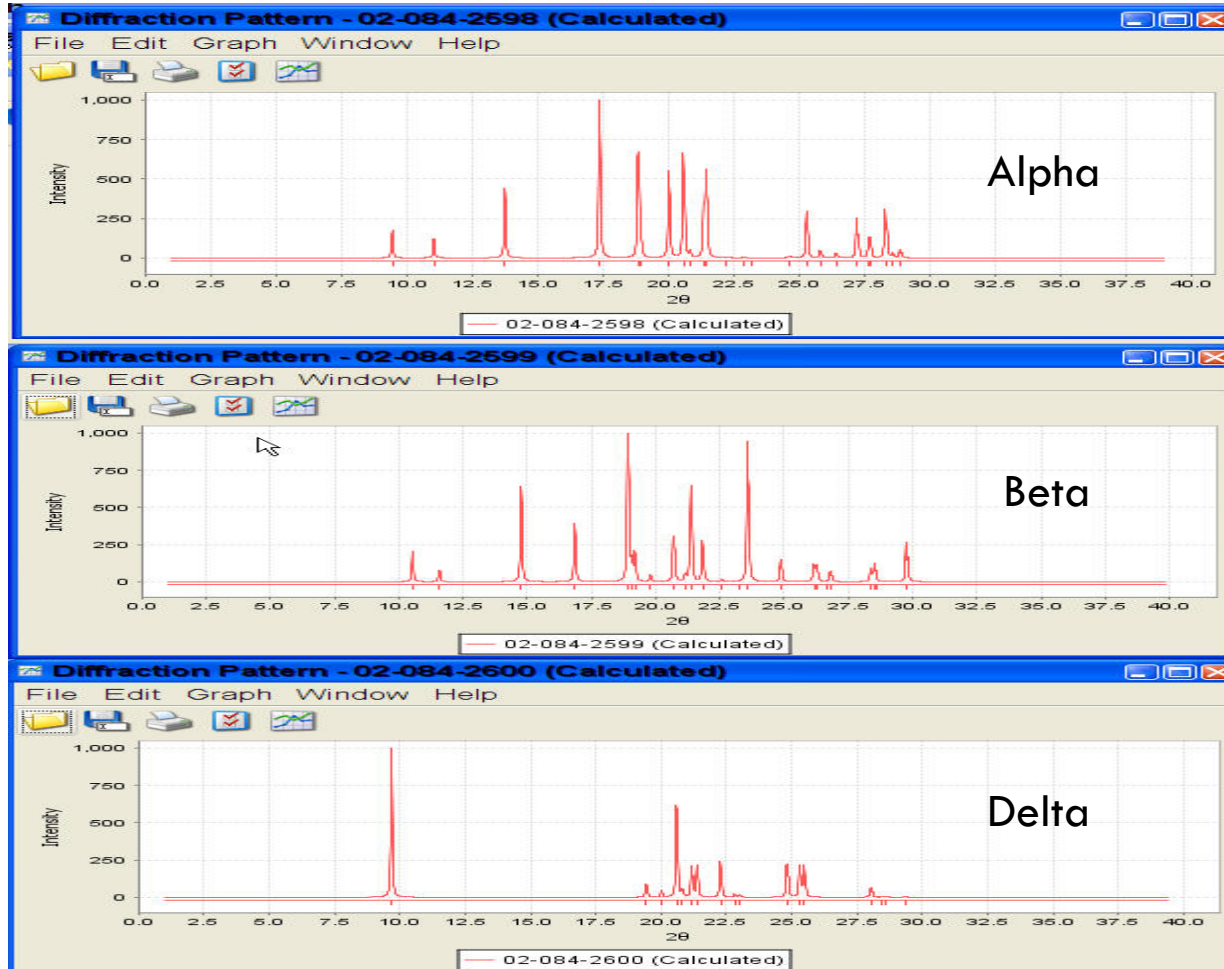
**Acetaminophen C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>**

**NIST SRM\_640C**

**Silicon Powder - line position and  
Line shape for powder diffraction**

# Mannitol Polymorphs

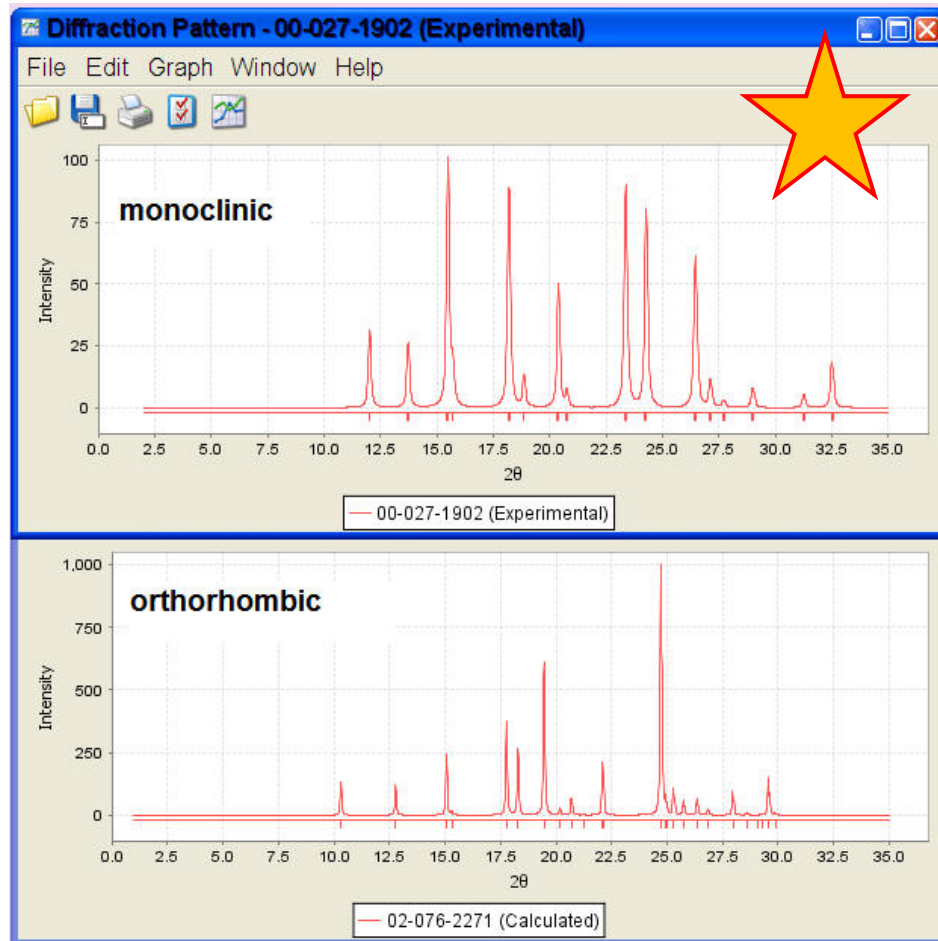
-both powder and single crystal data



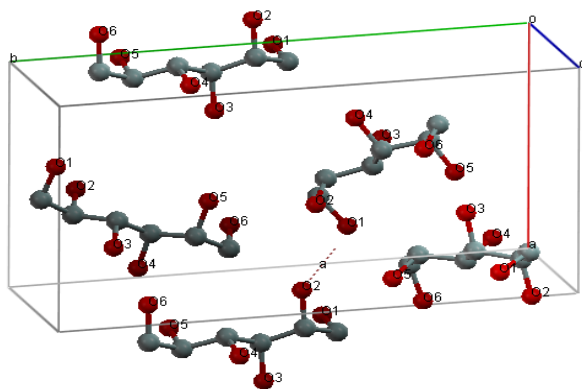
# Acetaminophen

ICDD  
PDF-/Organics 2009  
two known polymorphs

Form I - Monoclinic  
Form II - Orthorhombic



# Round Robin – Crystal Structures



**$\beta$  – D-Mannitol**  
**02-069-8458**

Orthorhombic  
A= 8.6940(70)  
b= 16.9020(80)  
C= 5.5490(60)  
P212121 (19)  
Z= 4.00  
V= 815.40

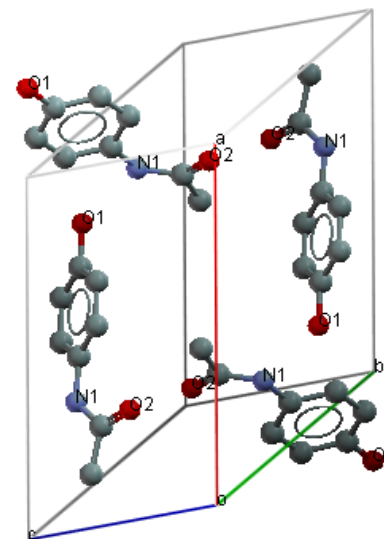
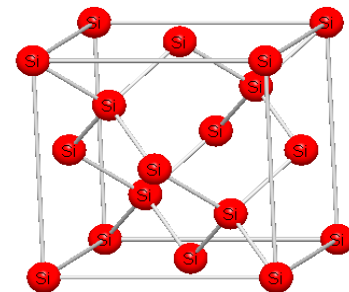
**15 References**

Acetaminophen  
**Polymorph Form I**  
**02-063-1190**

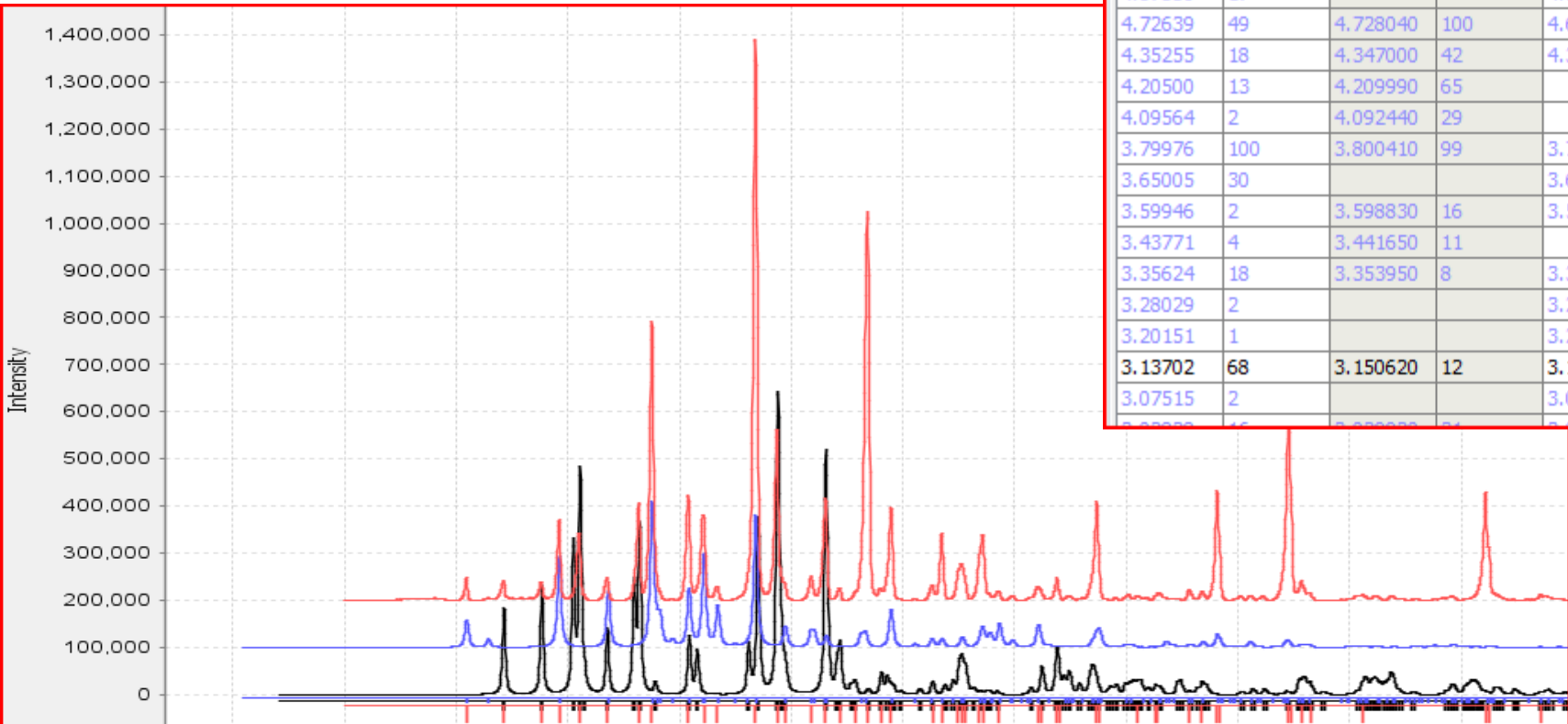
Monoclinic  
A= 12.7630(60)  
B=9.2500(40)  
c=7.0820(20)  
 $\beta$  =115.52(3)  
P21/a (14)  
Z= 4.00  
V=754.51

**12 References**

Silicon  
Cubic  
A = 5.431  
Fd-3m  
Z=8  
V=160.19



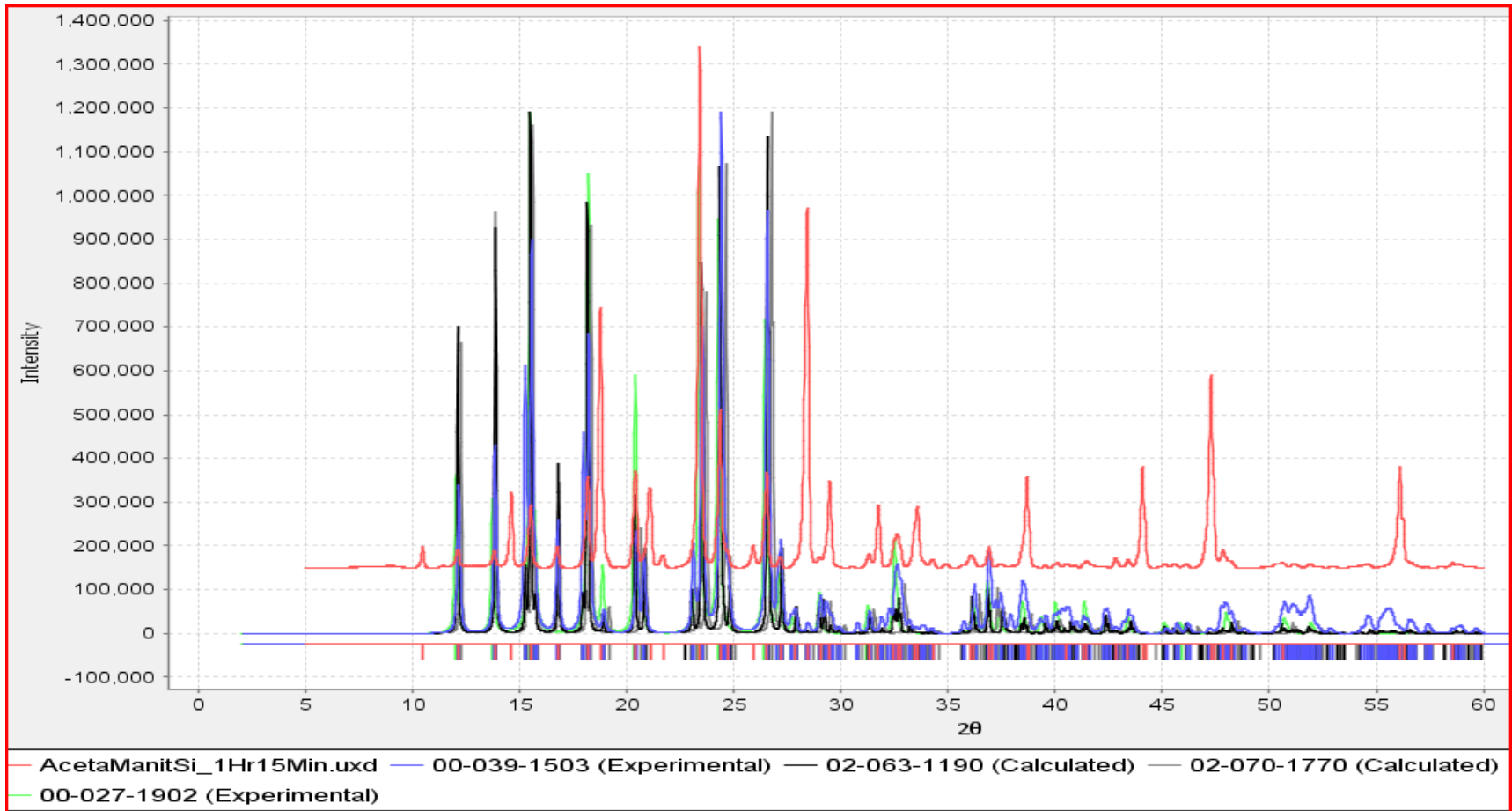
# Search/Match to identify polymorphs



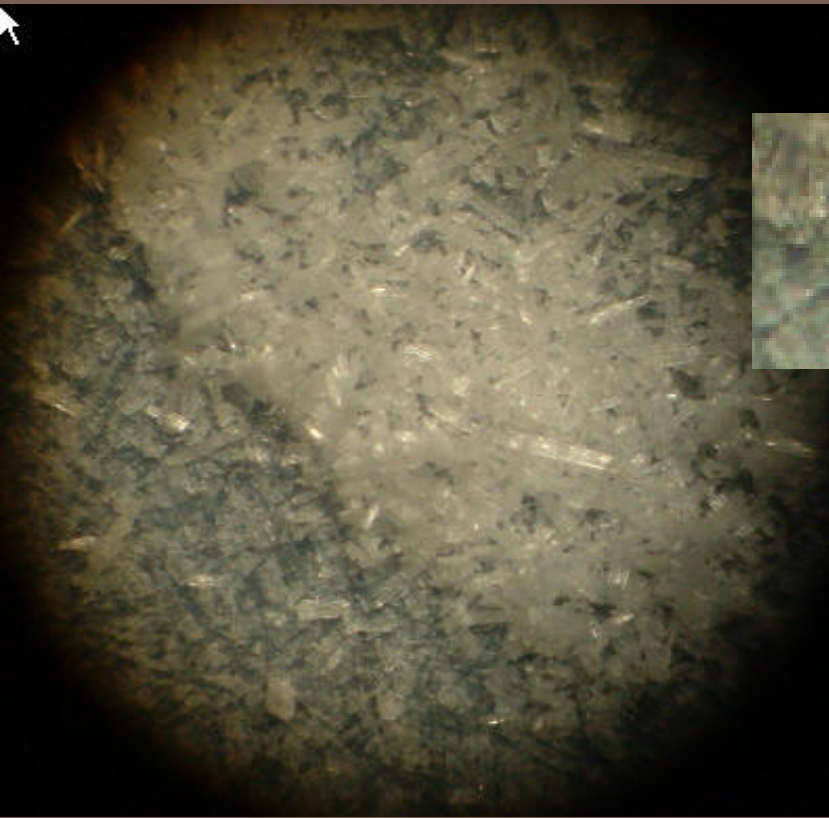
Lines (48 of 56)

Ex d(Å) ▼	Ex I	P1 d(Å)	P1 I	P2 d(Å)	P2 I
8.44428	3	8.451000	18		
7.29457	3			7.300000	29
6.40230	3			6.408000	37
6.05661	14	6.059850	60		
5.70564	11			5.706000	71
5.28670	3	5.272140	37	5.290000	21
4.87330	17			4.872000	56
4.72639	49	4.728040	100	4.693000	4
4.35255	18	4.347000	42	4.347000	21
4.20500	13	4.209990	65		
4.09564	2	4.092440	29		
3.79976	100	3.800410	99	3.784000	59
3.65005	30			3.649000	100
3.59946	2	3.598830	16	3.599000	8
3.43771	4	3.441650	11		
3.35624	18	3.353950	8	3.357000	77
3.28029	2			3.280000	15
3.20151	1			3.203000	4
3.13702	68	3.150620	12	3.138000	2
3.07515	2			3.076000	7

# Top 4 best statistical fits – all form I

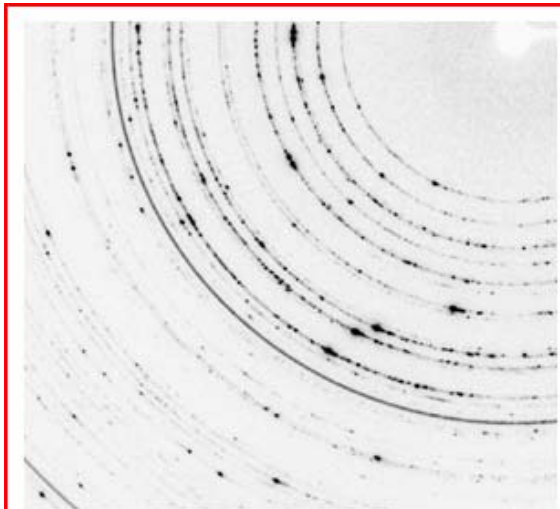


# ROUND ROBIN - CRYSTALLITES



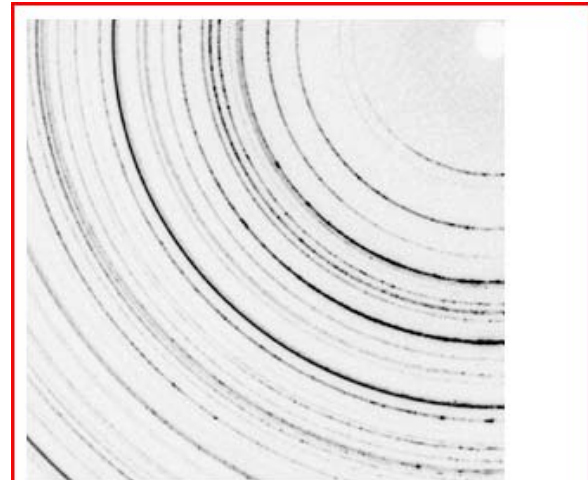
**Acetaminophen**

# Granularity



ASi - A + Silicon  
Spotty rings.

Acetaminophen



MSi - M + Silicon  
Strong texture and some spottiness.

# Constraints used in the round robin

- Specimen prep – none
- Instrument used – none
- Optics settings – none
- Data processing programs – none
- Data treatment –none
  
- ICDD did ask that all the above steps be recorded

# Experimental Parameters

id	Specimen	system	Goniometer	wavelength	spin	software
0	Cavity	Bruker D8	theta-theta	CuKa1/CuKa2	Yes	GSAS
2	cavity	Bruker D8	theta-theta	CuKa1/CuKa2	yes	FullProf
3	capillary	TTRAXIII(Rigaku)	theta-theta	CuKa1/CuKa2	no	GSAS
4	zero-background	ARL X'tra XRD	theta-theta	CuKa1/CuKa2	yes	Jade 8.5
5	Cavity-side filled	Rigaku D-Max III B	vertical	CuKa1/CuKa2	no	riqas 5.0
9	0.4 mm OD, 0.01 mm wall thickness glass capillary	PANalytical X'Pert Pro MPD	theta-theta	CuKa1/CuKa2	yes	PANalytical High Score Plus v 2.2.0
11	The powder is filled between two Mylar foils with a 8mm diameter mask	STOE STADIP transmission diffractometer		Cu-Ka1	yes	Rietveld program SiroQuant®, Version 3.0
12	cavity	PANalytical X'Pert	theta-theta	CuKa1/CuKa2	yes	Rietveld
17	cavity	PANalytical X'Pert ProMPD	theta-2theta	CuKa1/CuKa2	yes	Sieve+
18	cavity	RigakuD5005	theta-2theta		no	jade 8.0

# Round Robin Data

## Analysis Program

PolySnap

X'Pert HighScore Plus

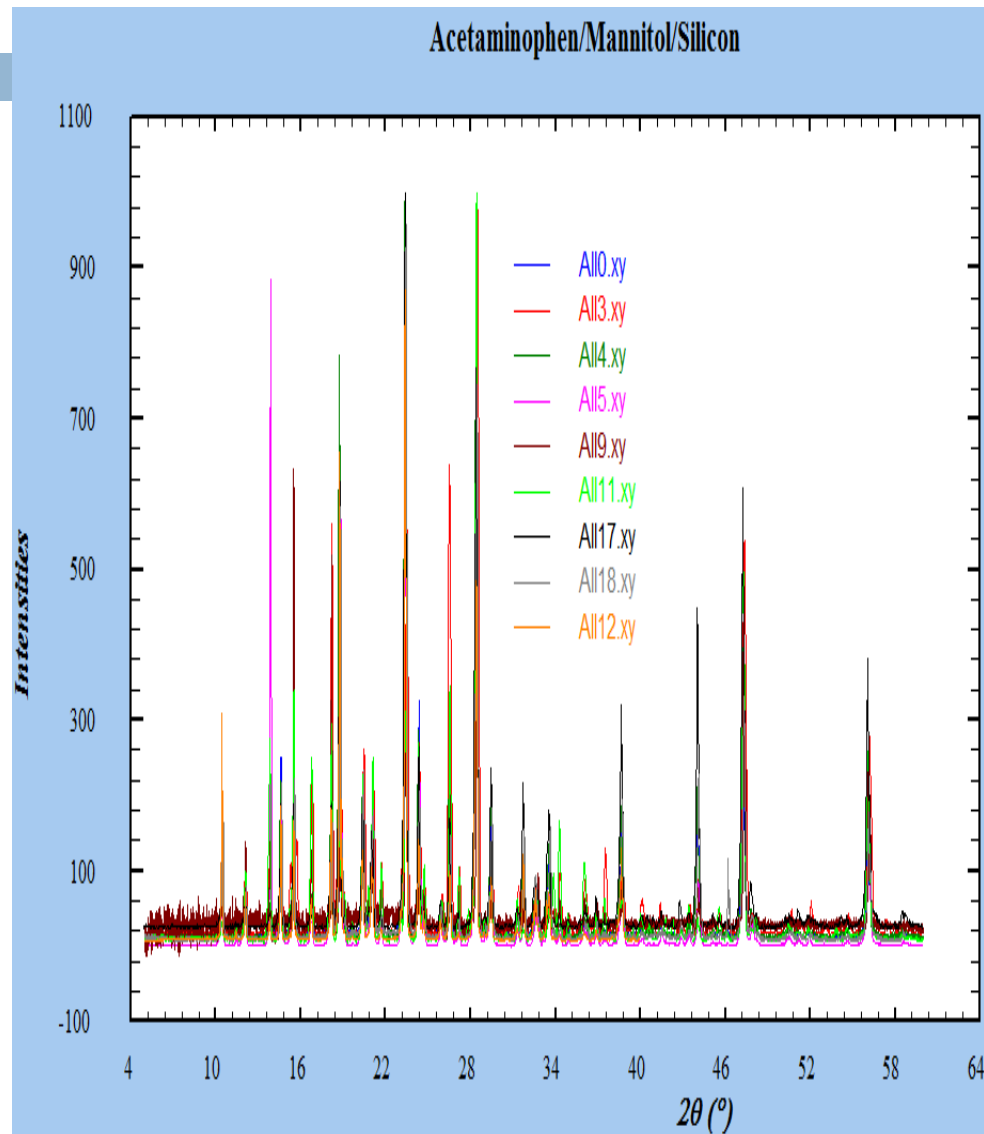
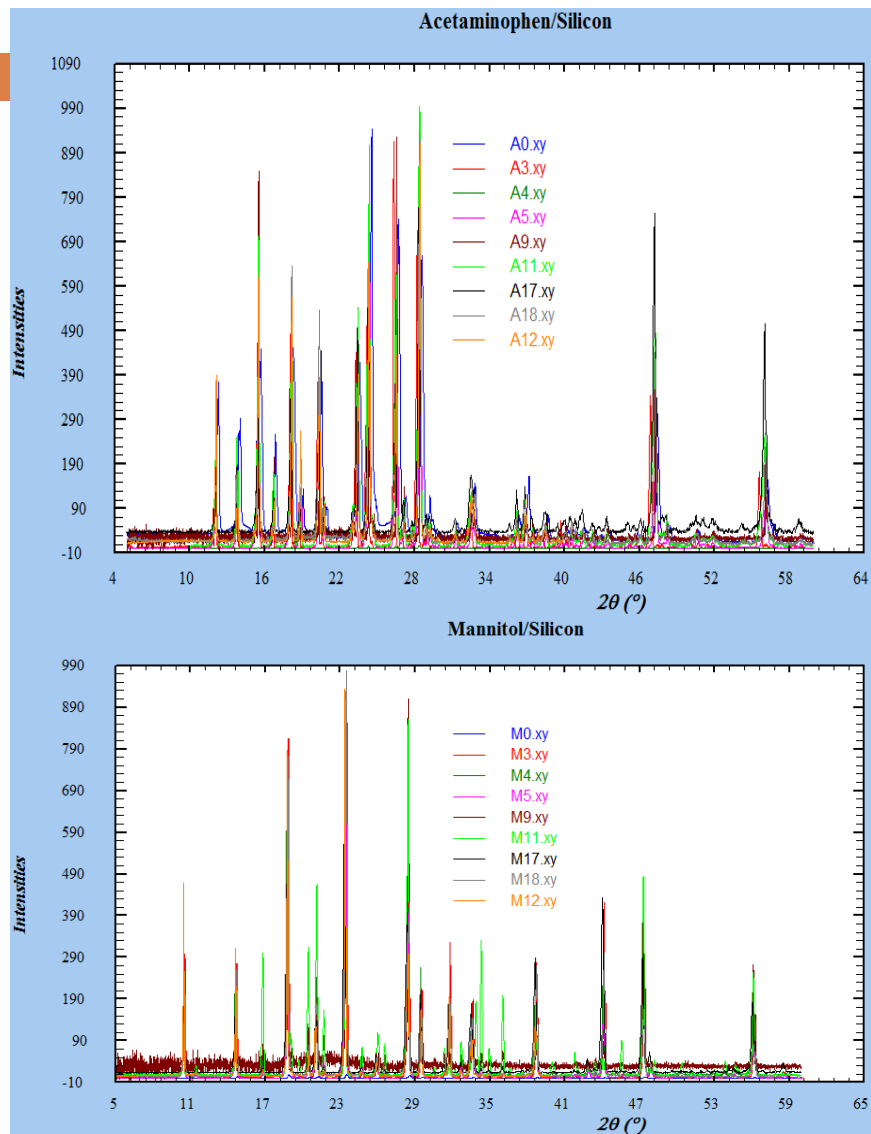
## Participants

Labs 1, 4, 5, 9, 11, 17, 18

Labs 1, 3, 4, 5, 9, 11, 17, 19

63 Total Data sets analyzed

# Round Robin Results



# Variables



Specimen preparation

Data Processing

- Selection of references
- Selection of refinement variables

# Cluster Analysis – 57/63 Data Sets

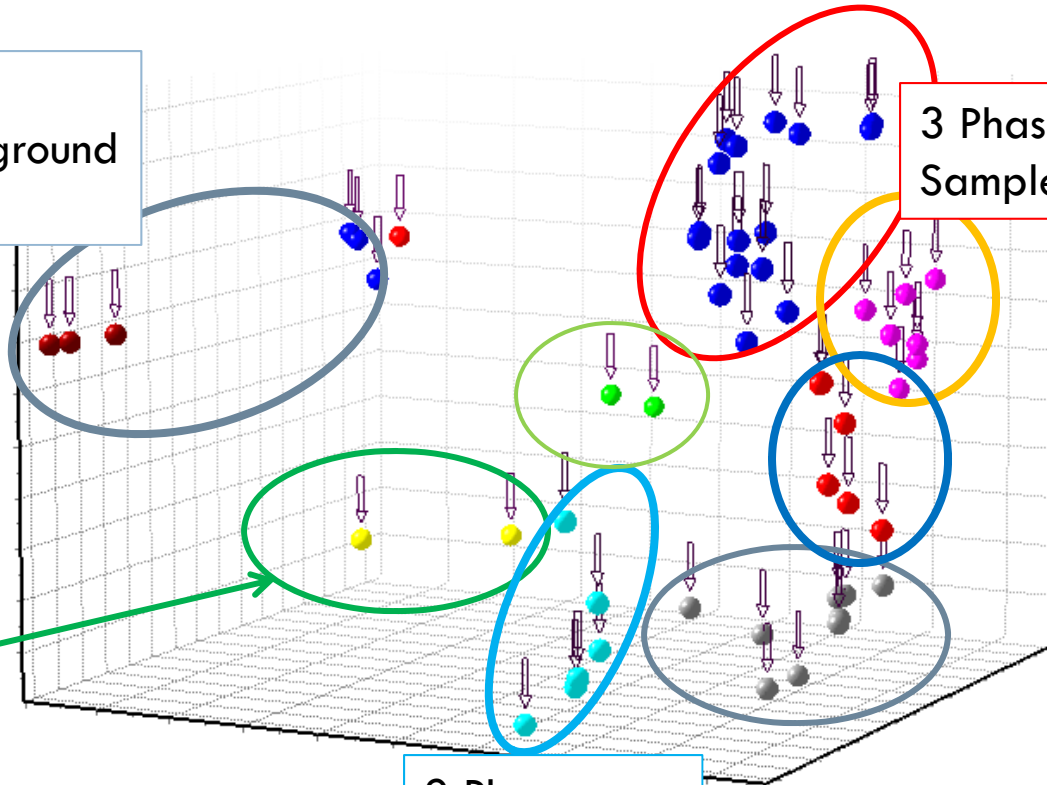
## Nine Clusters

Synchrotron  
w/wo background  
scatter

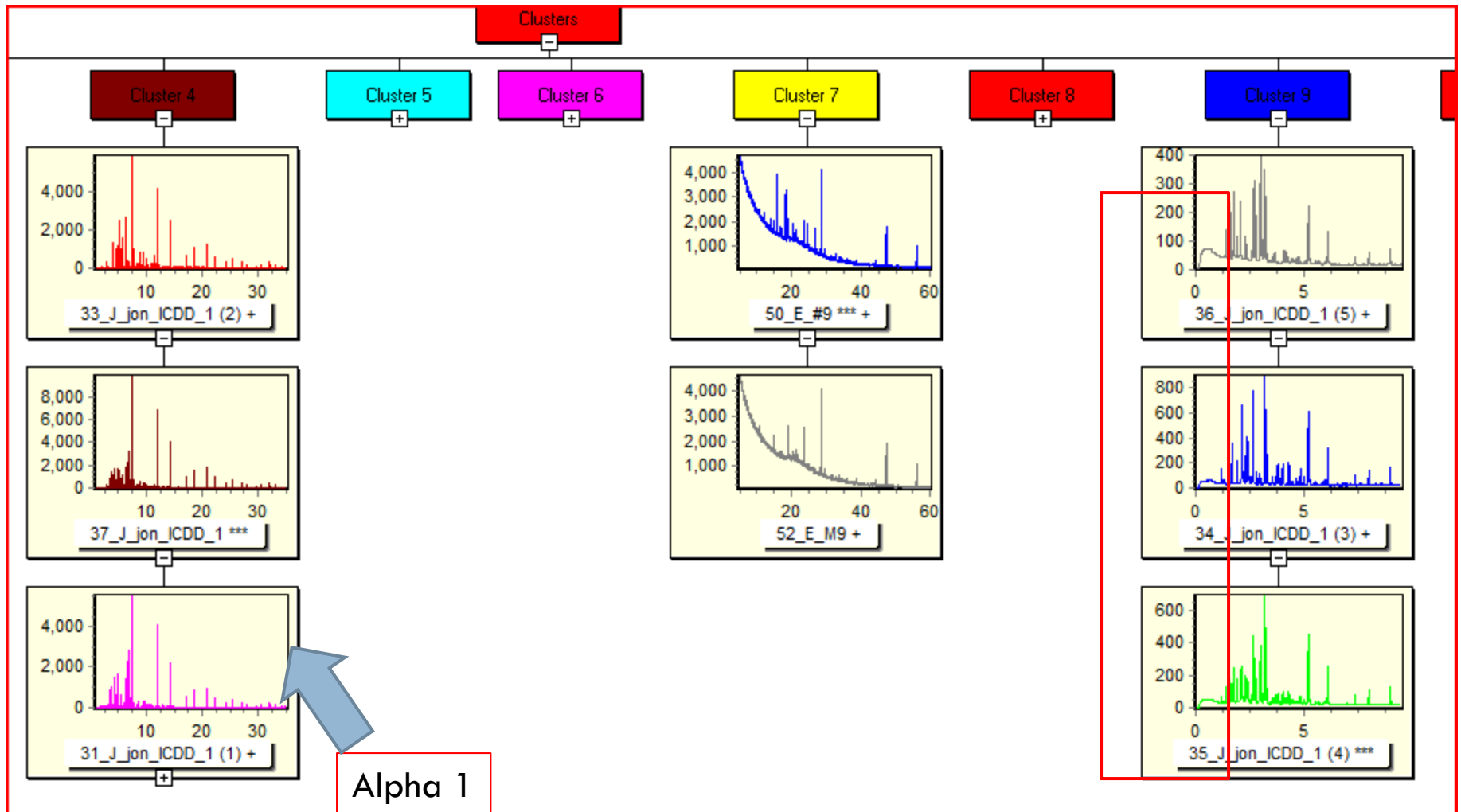
3 Phase  
Samples

Very High  
Background

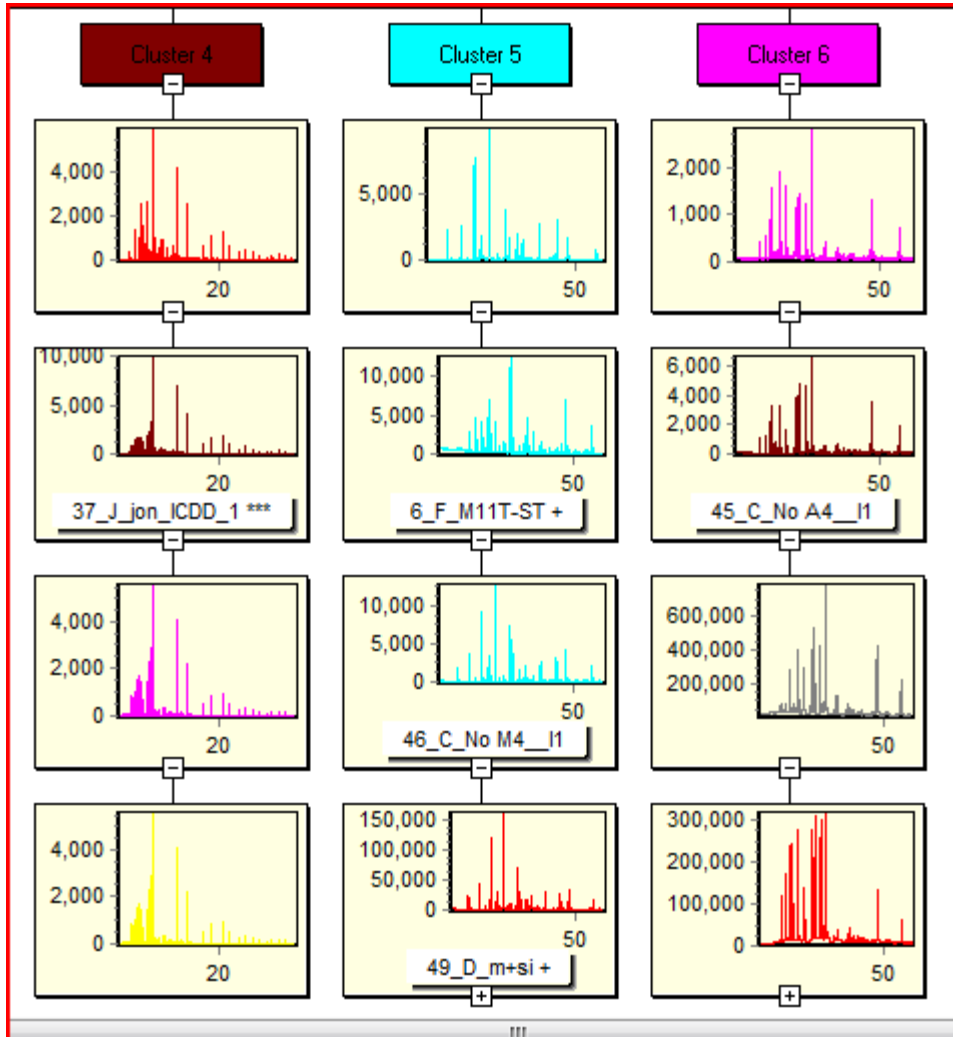
2 Phase  
Mannitol & Si



# Preparation/Instrument Clusters

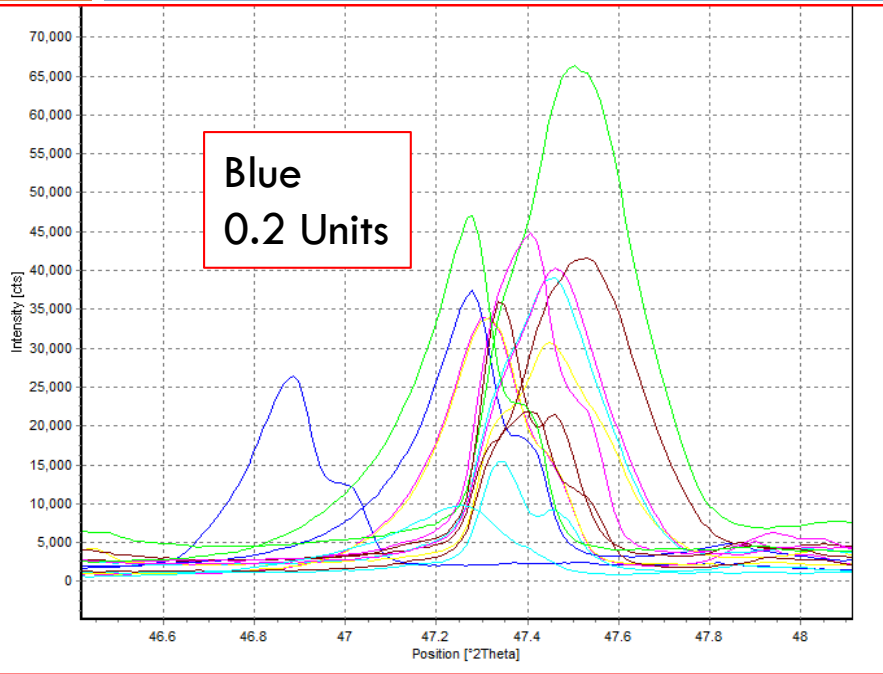


# Specimen Clusters



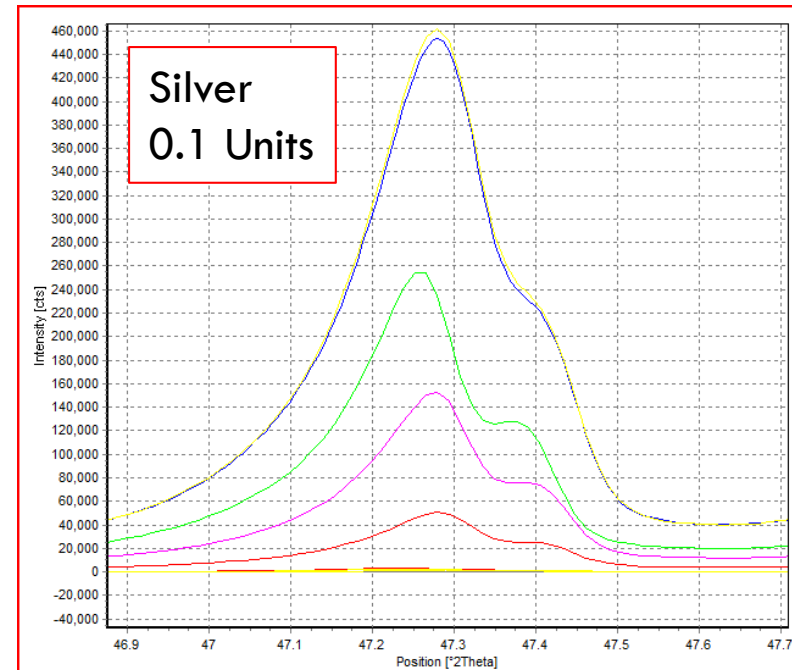
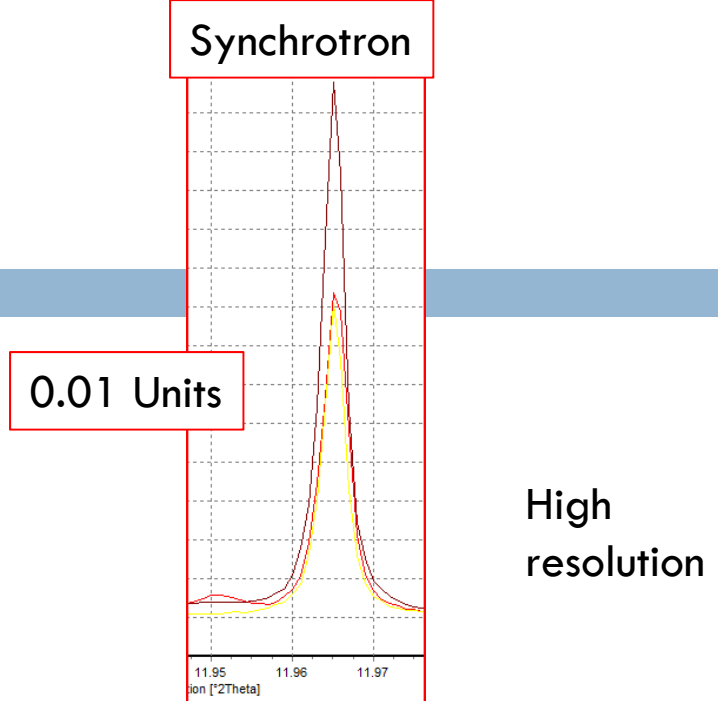
Note tremendous variations in Intensity scale

# Si 220 – Resolution



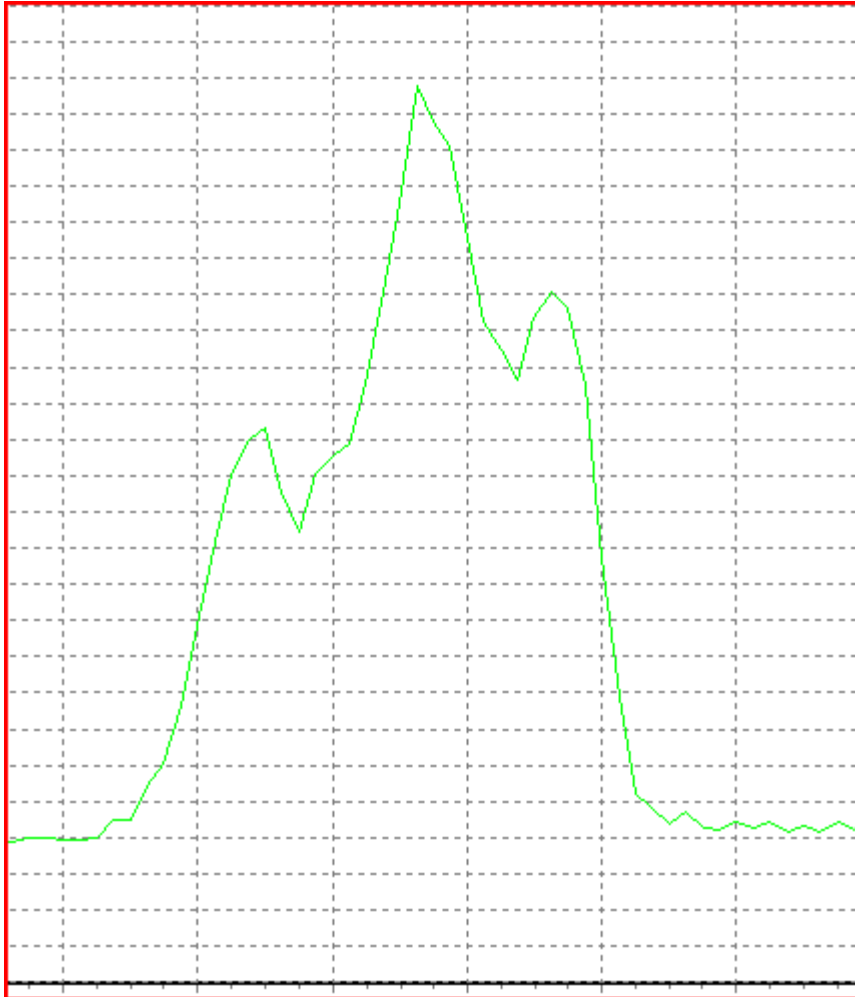
Mixed displacements, both low and high angle and low resolution

Blue data on left is probably a zero point error

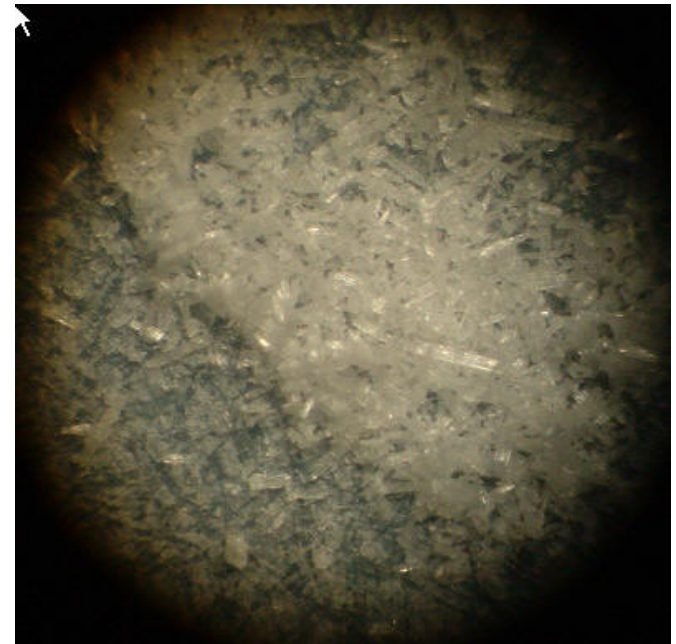




# Large grains – capillary mount

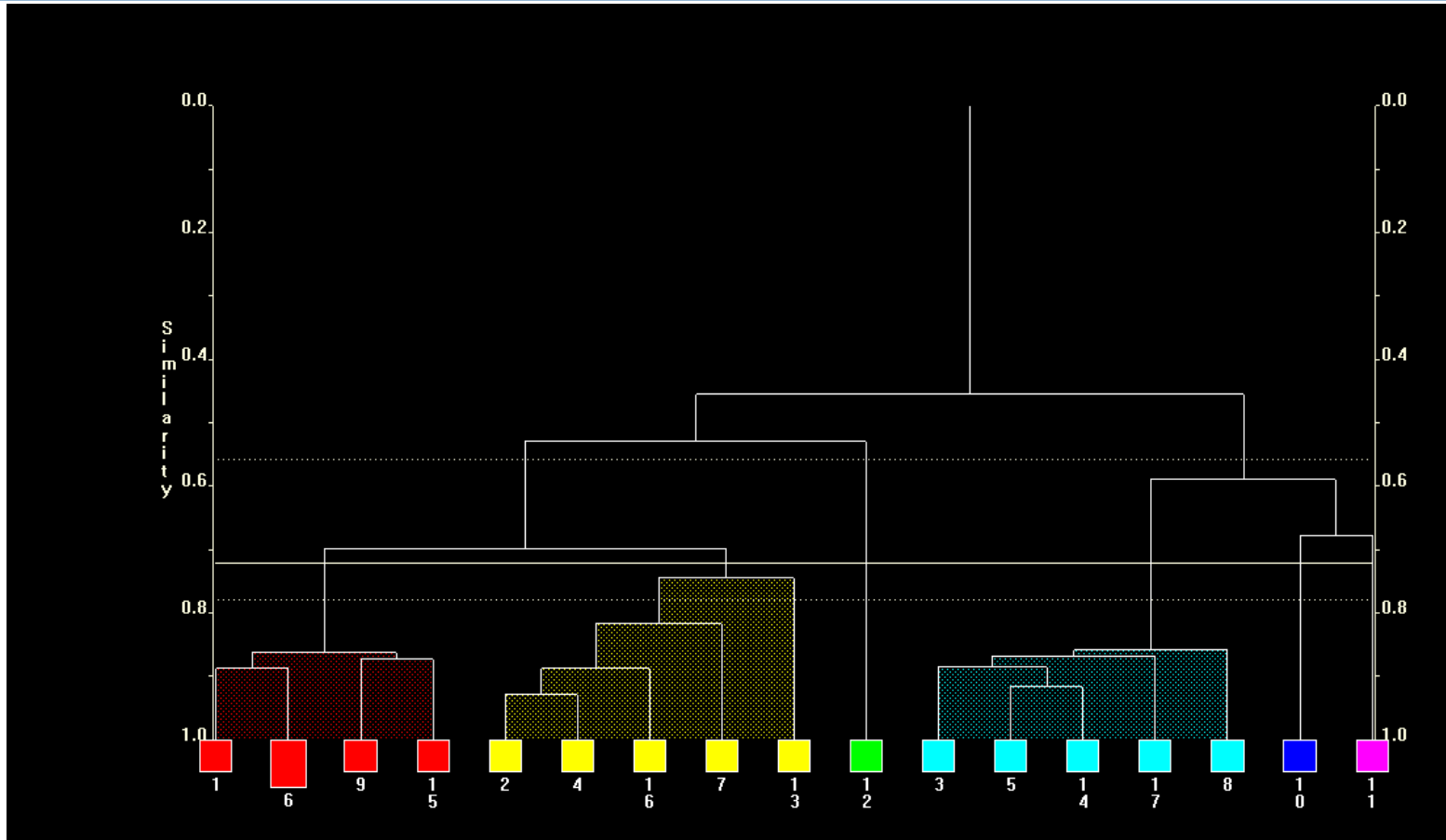


Large grains for acetaminophen



# First Pass 17 Data Sets

## - Dendrogram

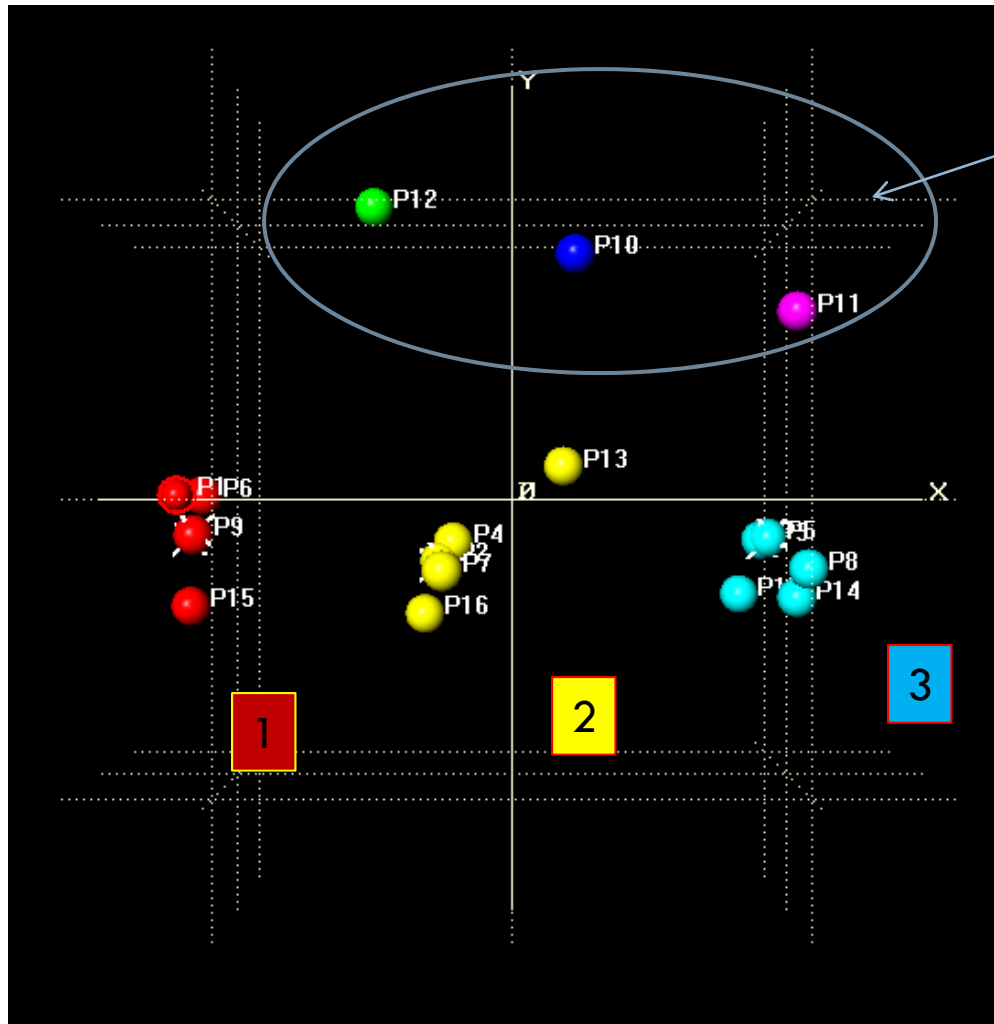


Mannitol &  
Silicon

Acetaminophen  
Mannitol & Si

Acetaminophen &  
Silicon

# First Pass – 17 Data Sets

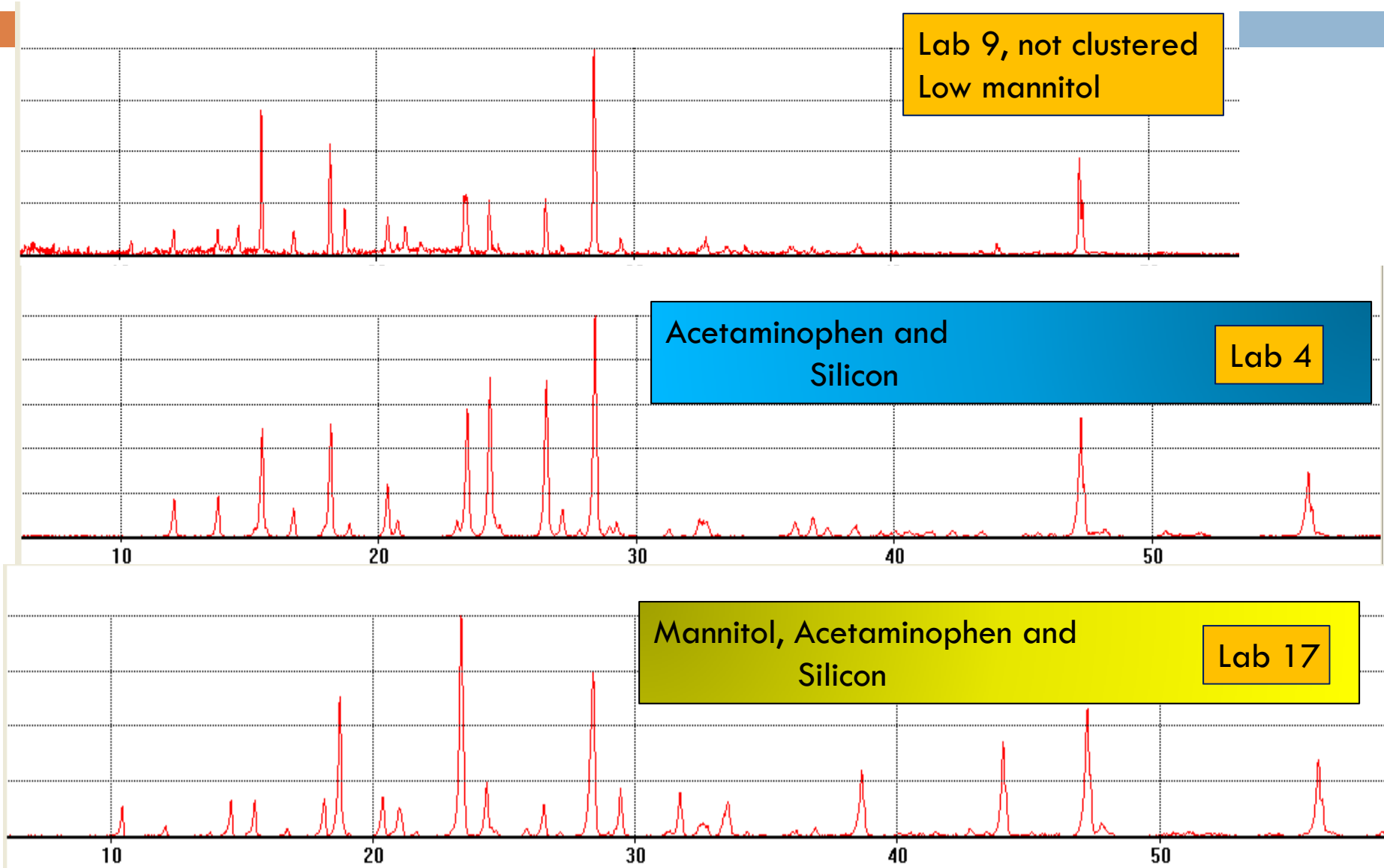


Different optics and specimen prep

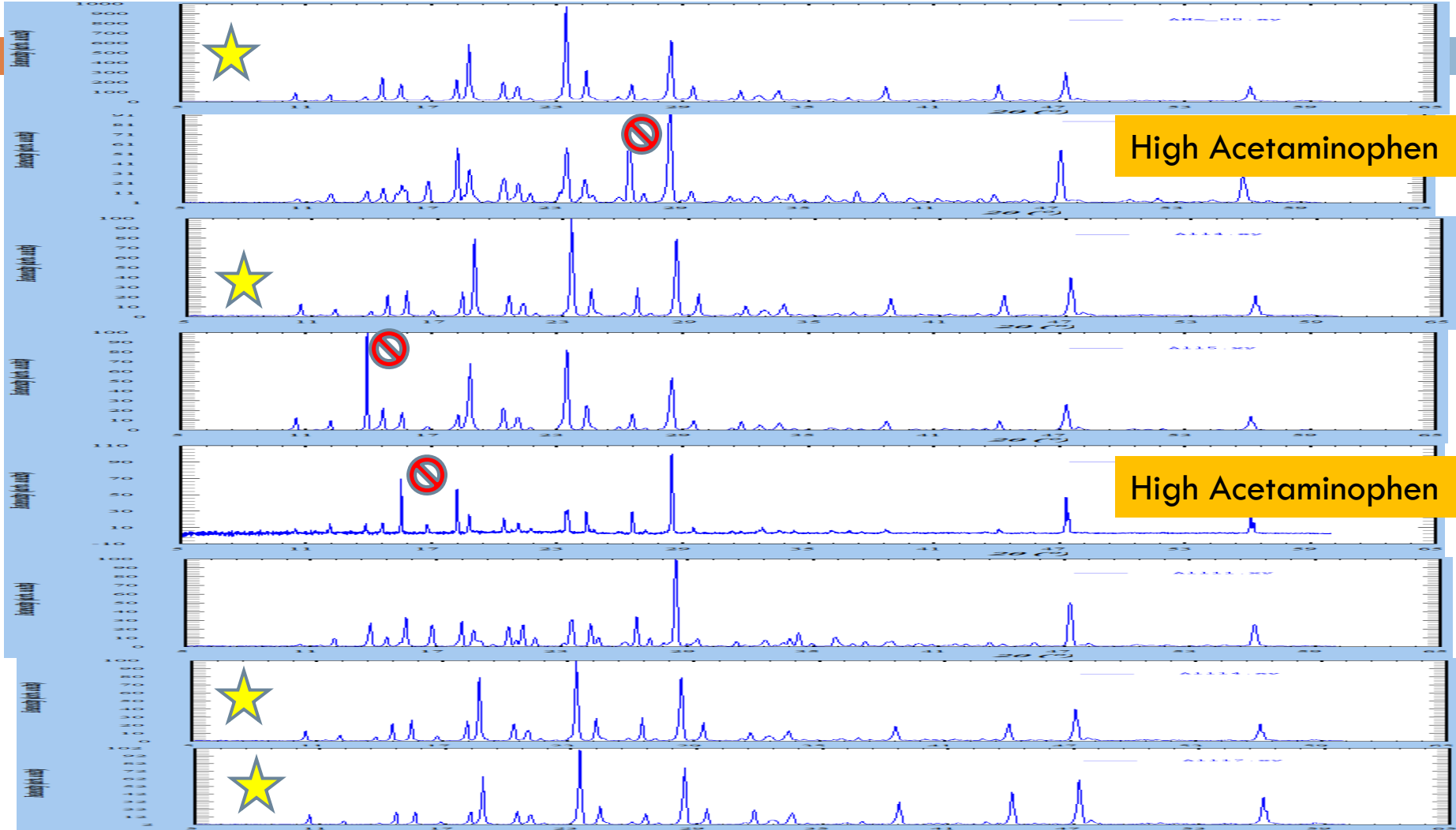
## Clusters

- 1) Mannitol and Silicon
- 2) Manitol, Acetaminophen and Silicon
- 3) Acetaminophen and Silicon

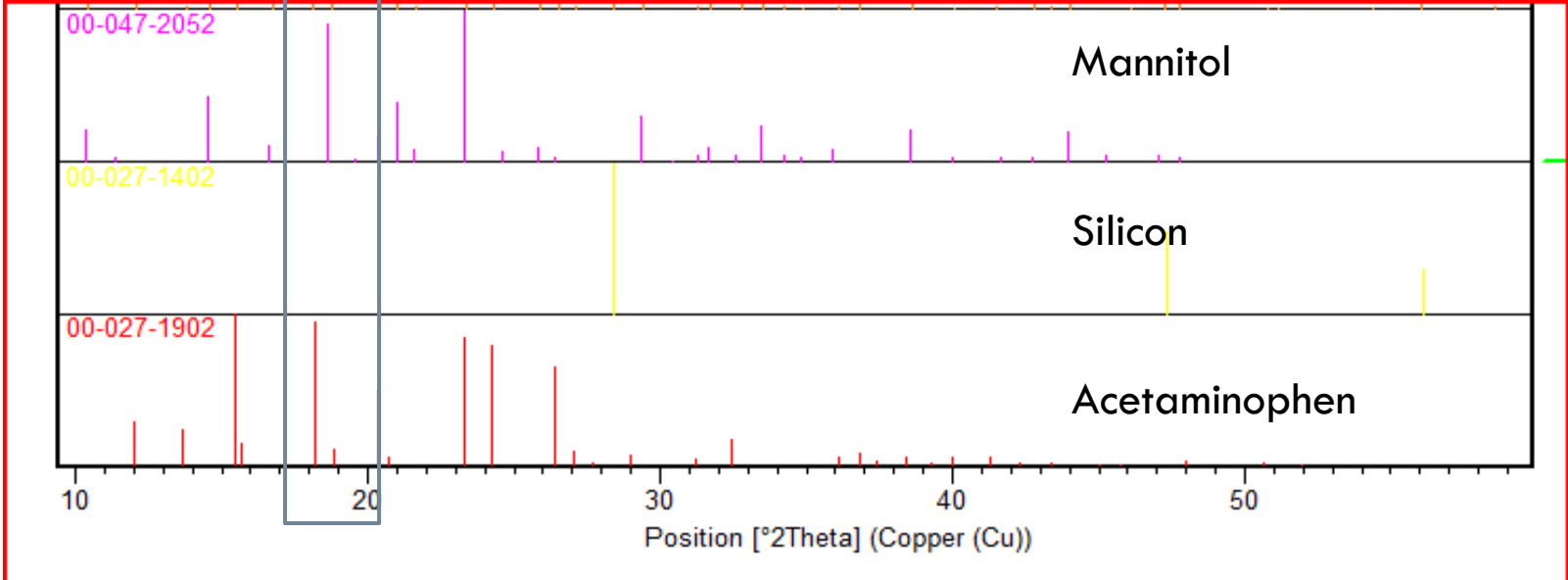
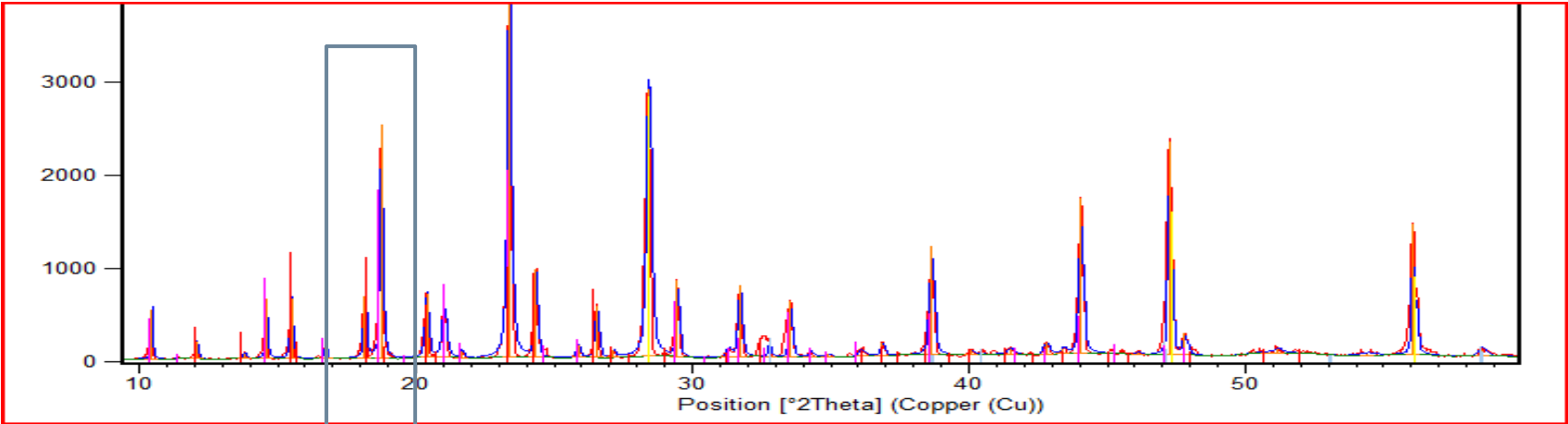
# Comparison of data



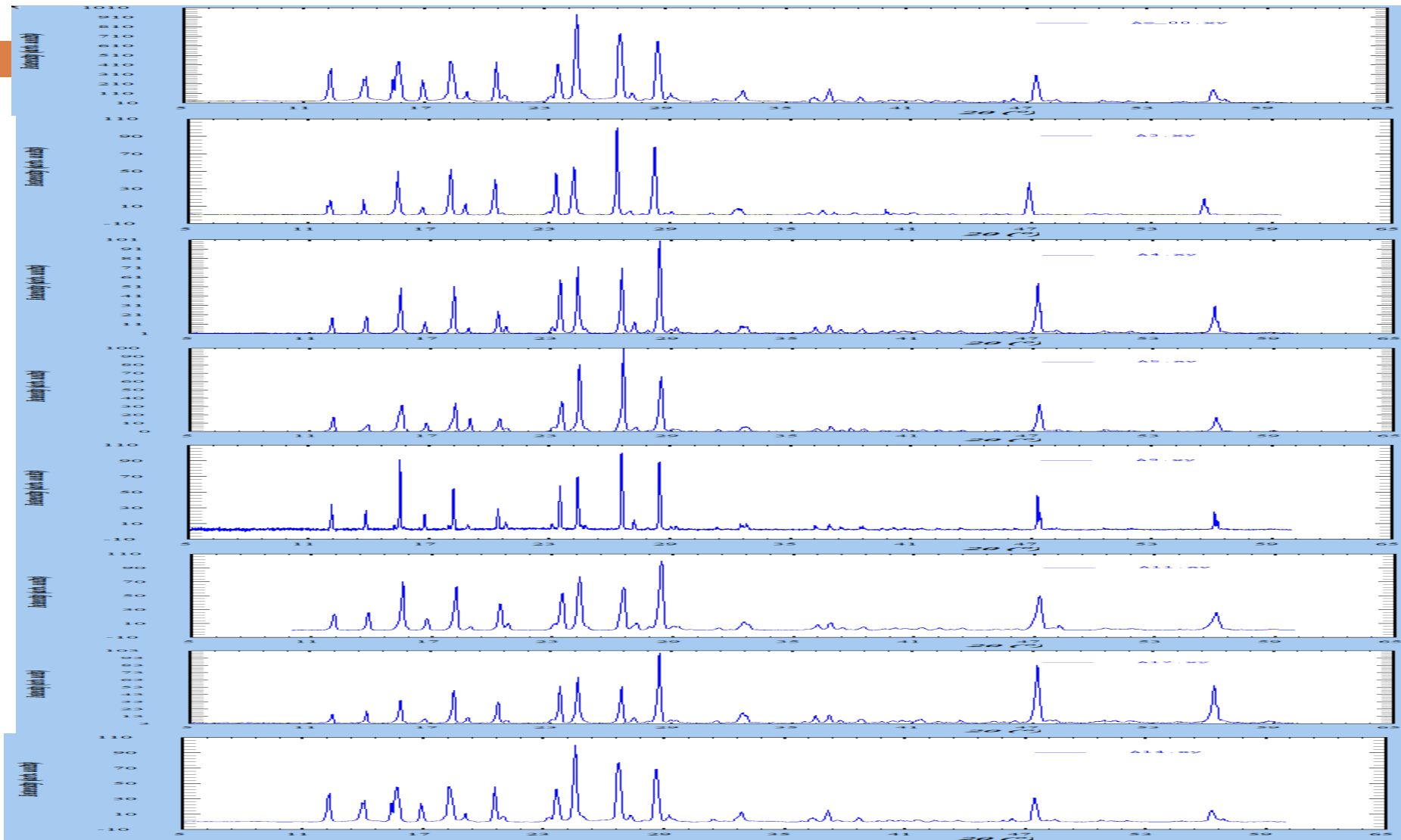
# Results Acetaminophen + Mannitol + Silicon



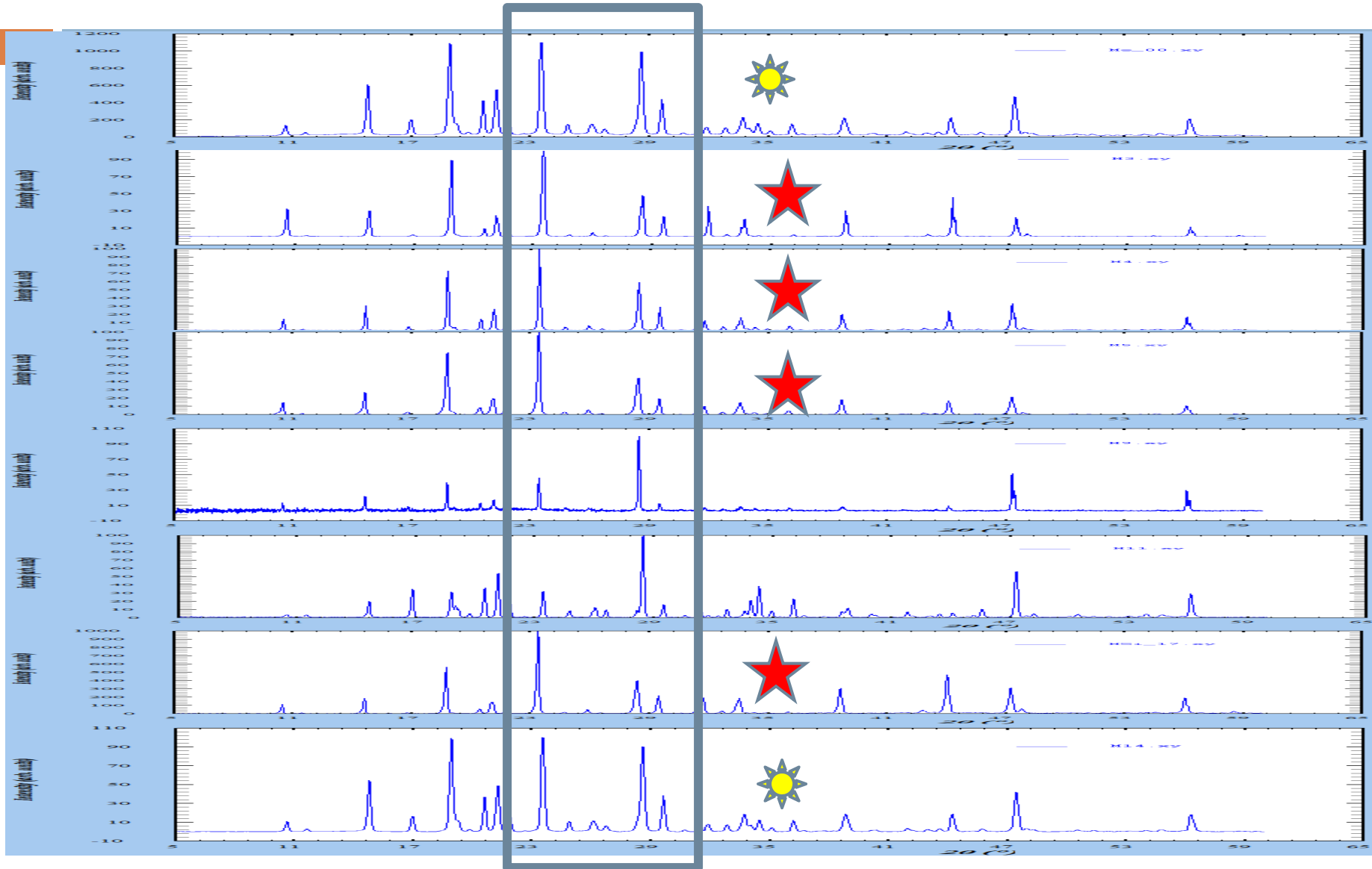
# Phase Identification



# Results – Acetaminophen + Silicon



# Results – Mannitol + Silicon



# Issues in specimen prep

Specimen displacement observed in most data sets  
- Was this corrected ?

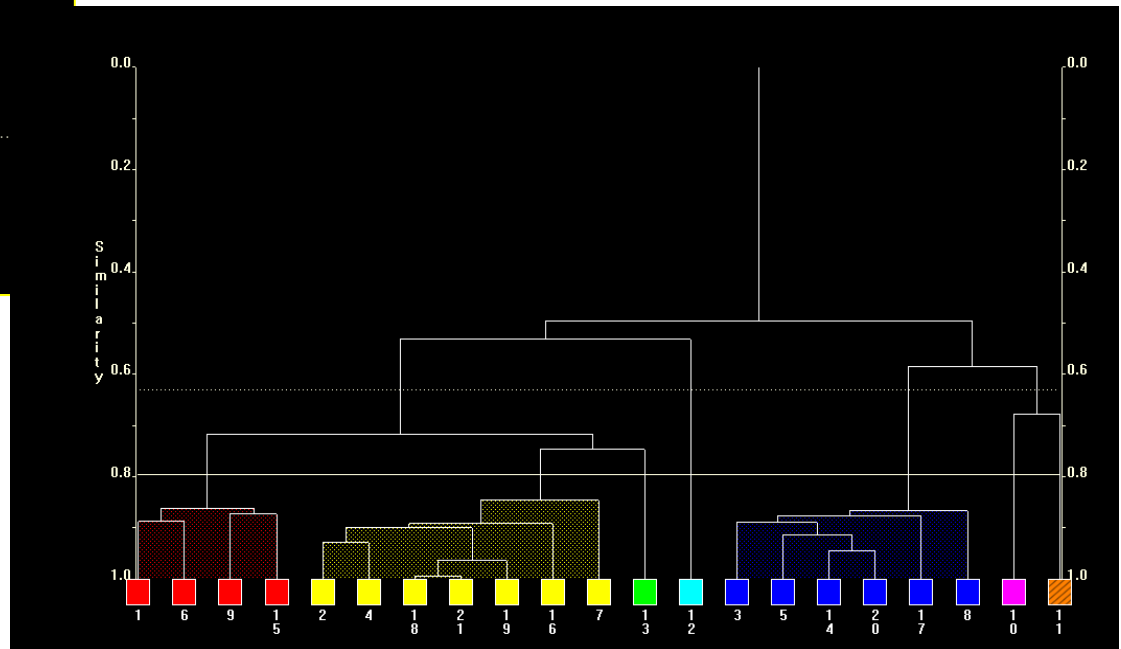
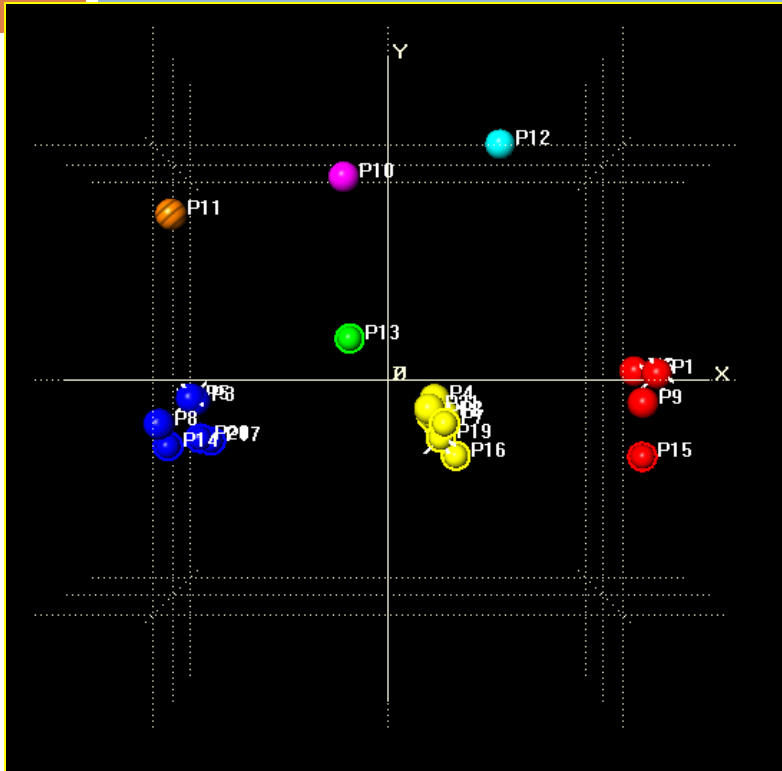
Specimen orientation observed

Non-representative specimens (obvious concentration differences)

Note: Ala Ron Jenkins

The sample is what is in the bottle. The specimen is what you present to the instrument.

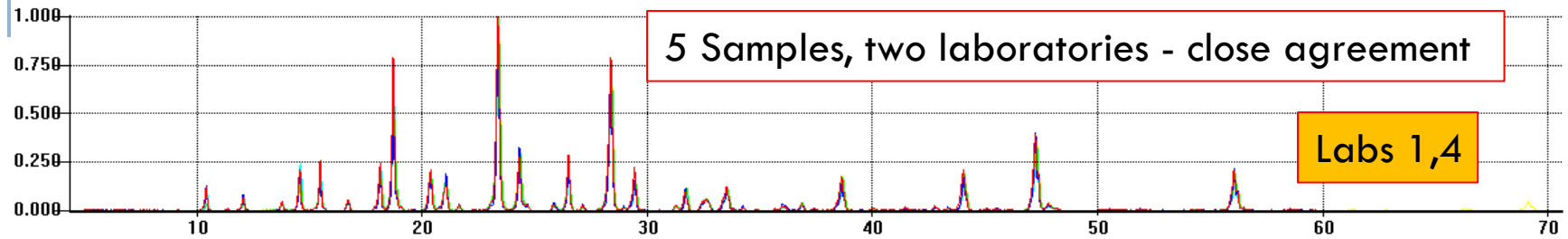
# 2<sup>nd</sup> Pass – 21 Data Sets



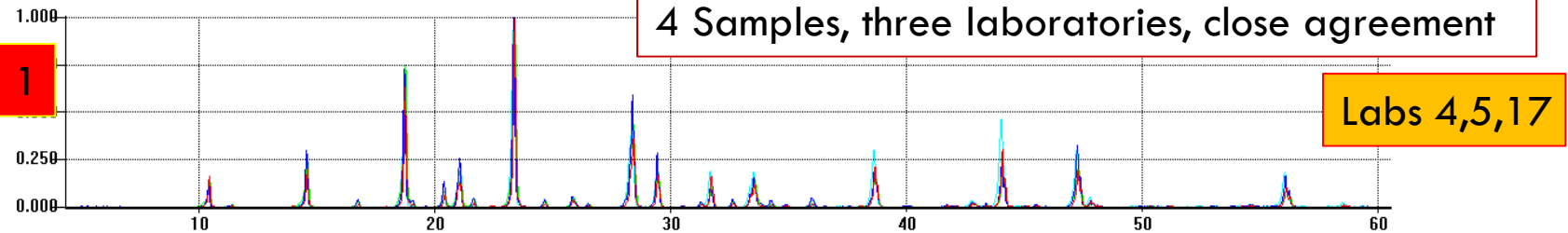
# Good News

Background stripped, scaled data

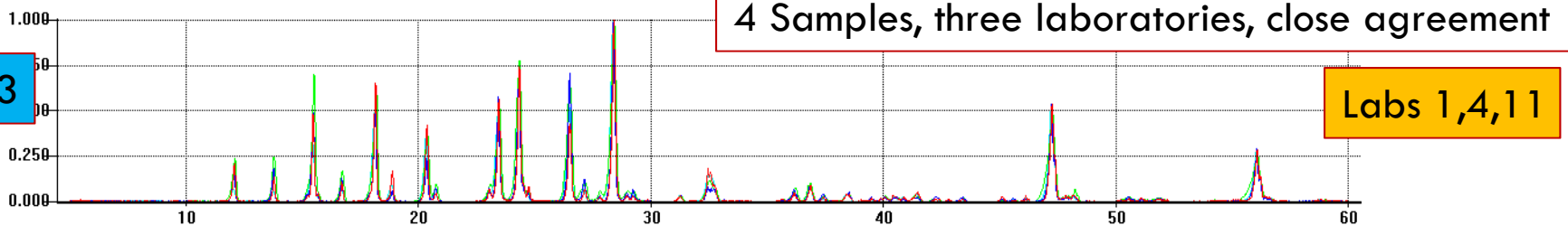
2



1



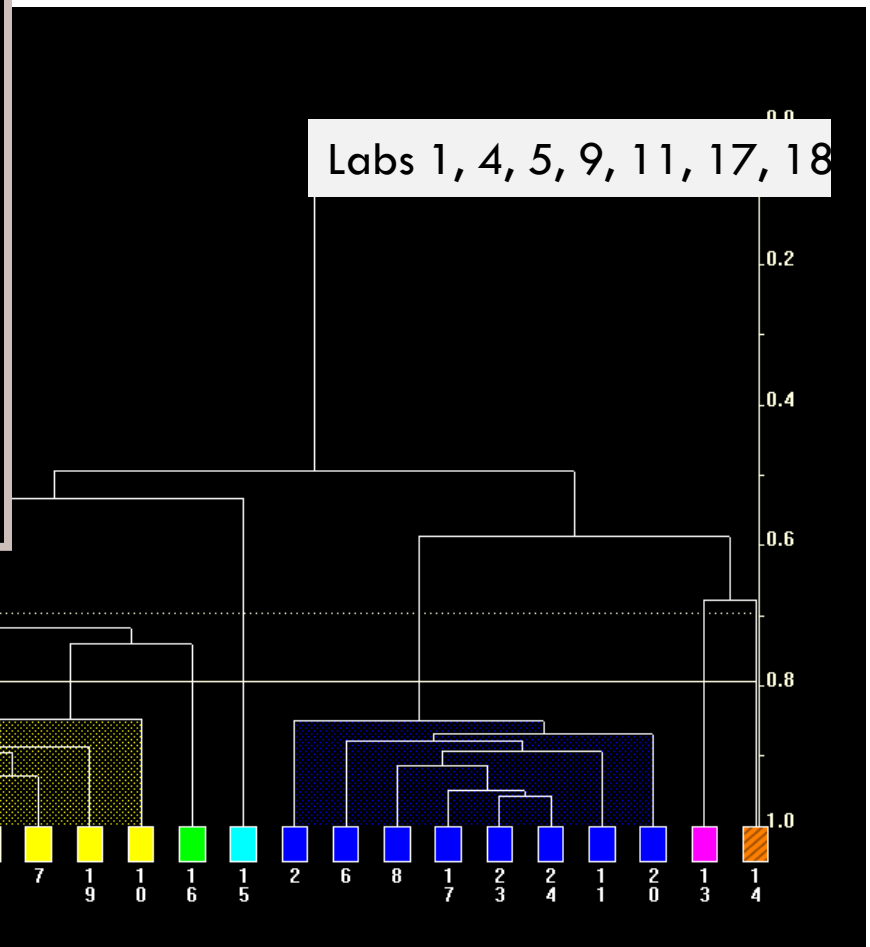
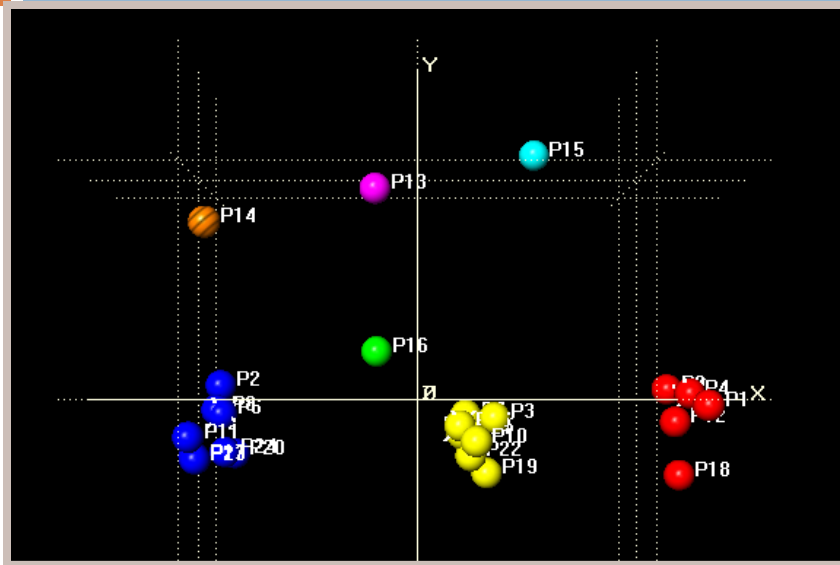
3



21 Data sets – 6 laboratories

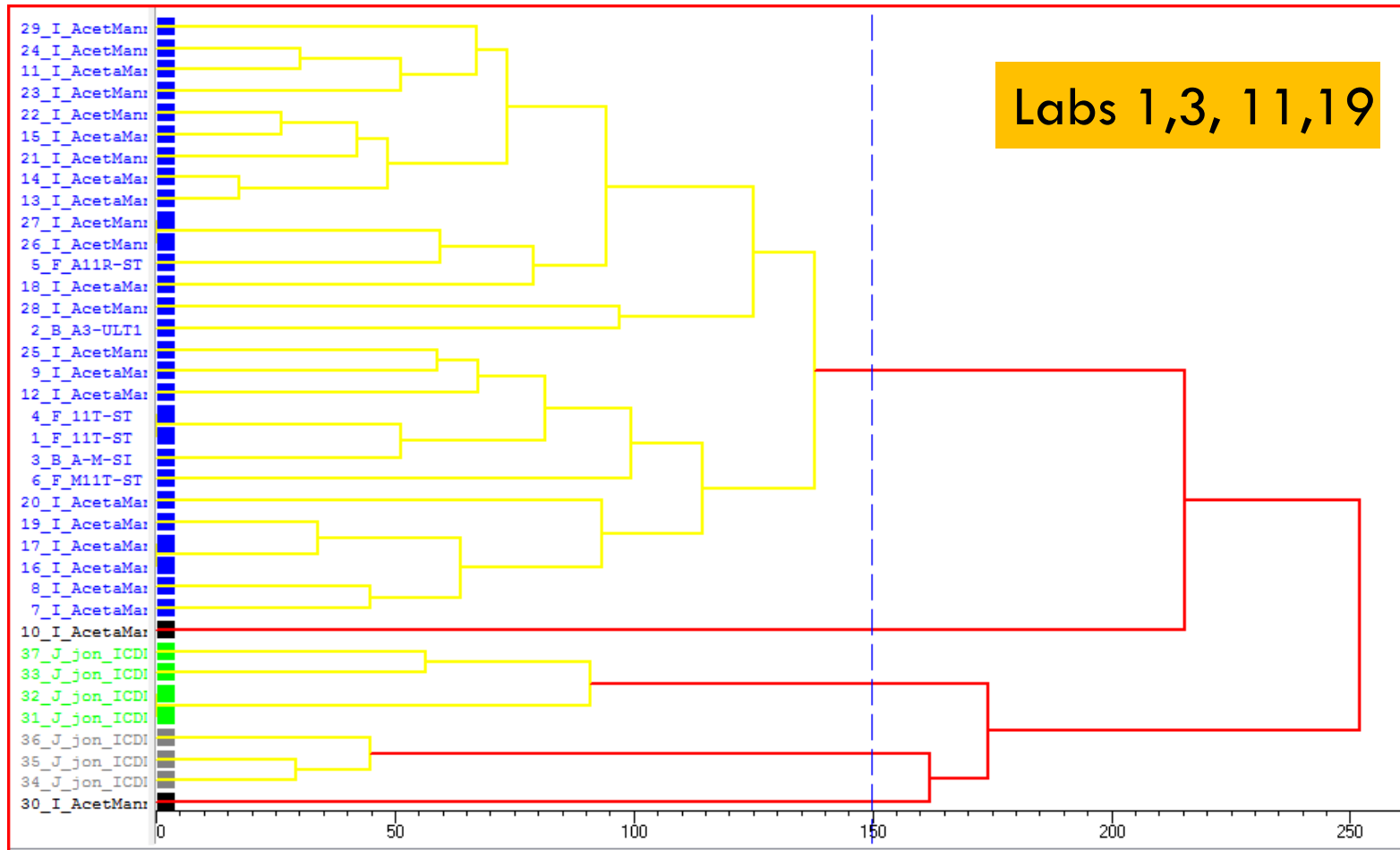
# 3<sup>rd</sup> Pass –

## 7 Laboratories, 26 Samples

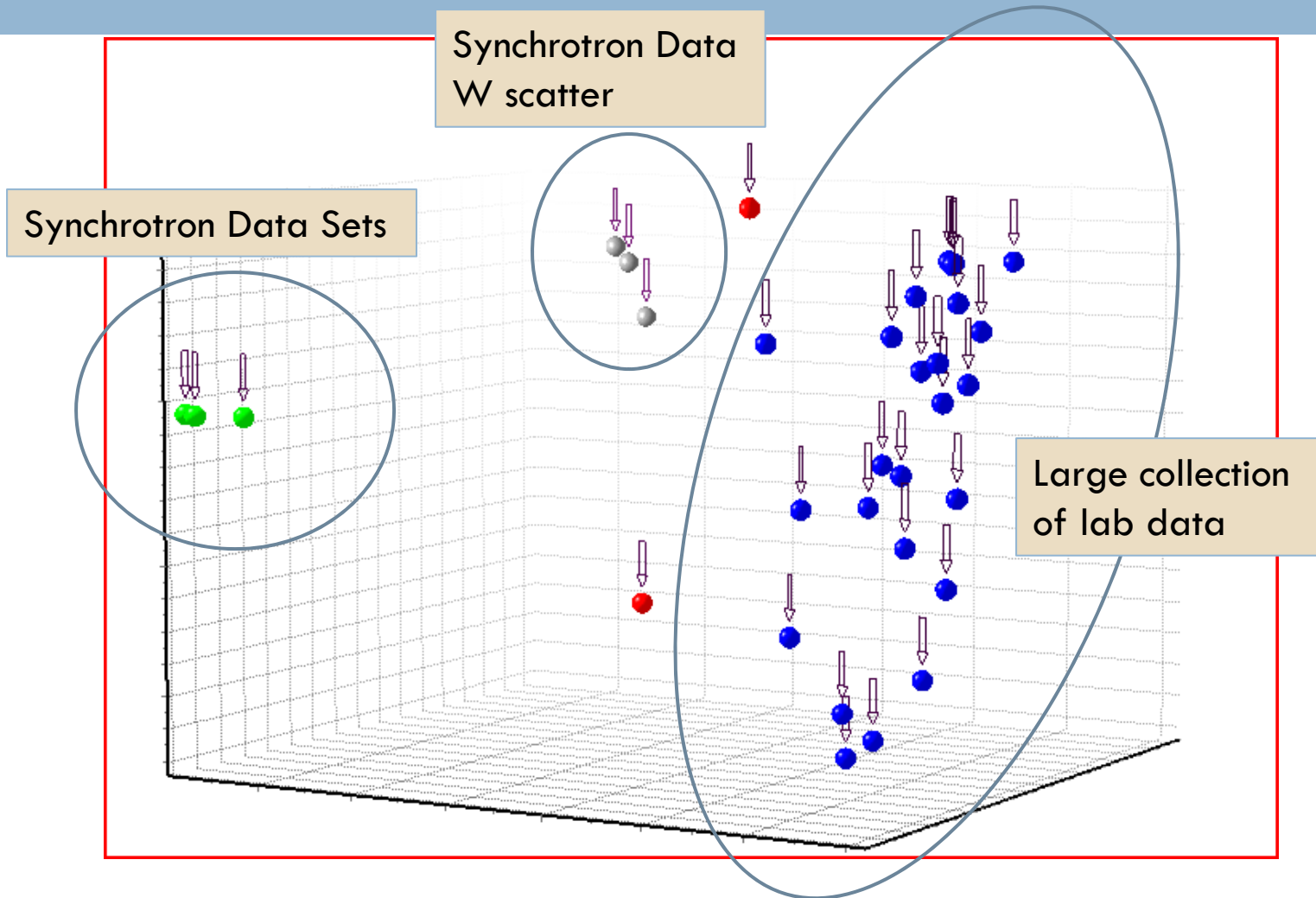


# HighScore Plus

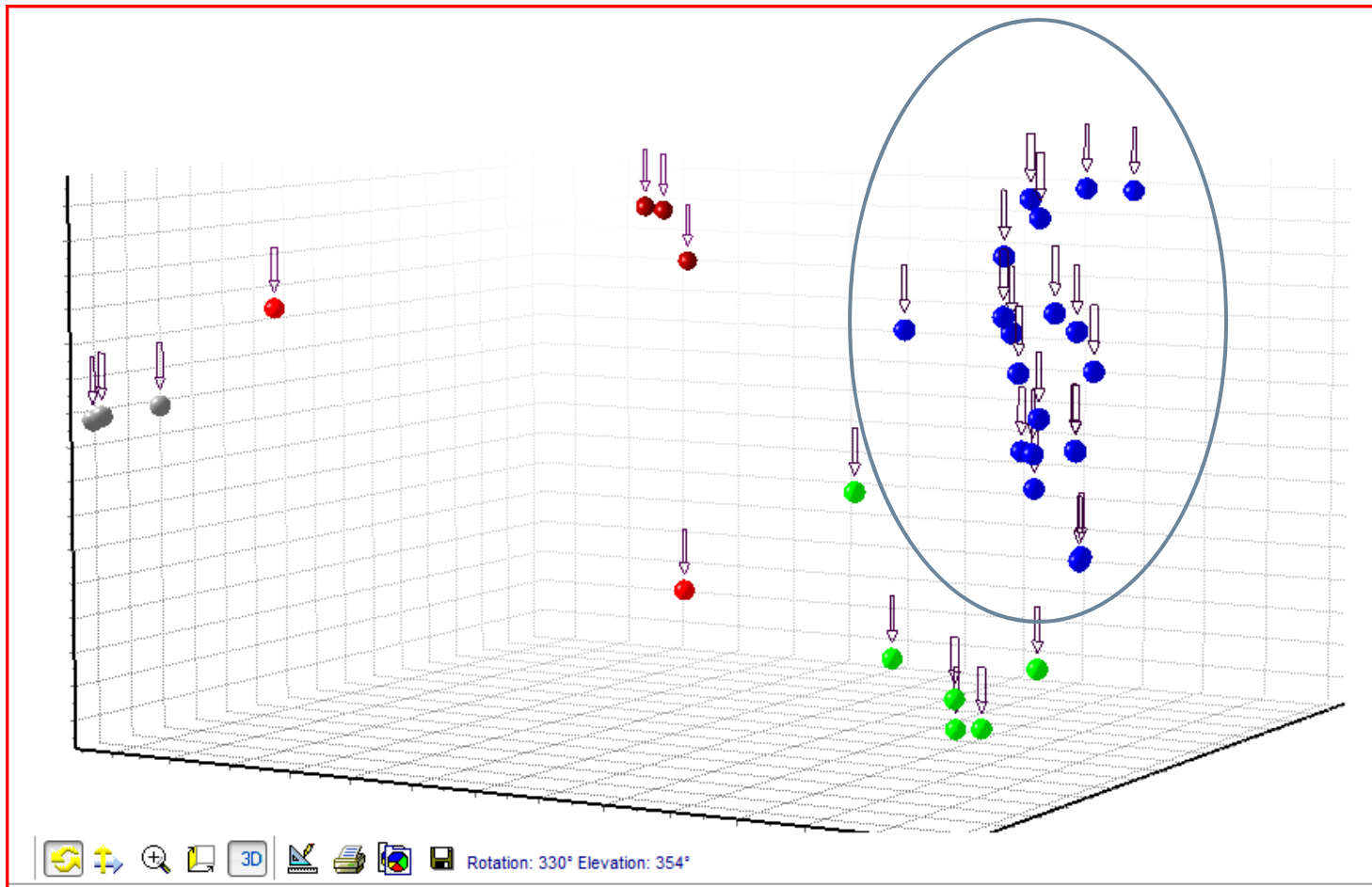
## 4 labs, 37 Samples



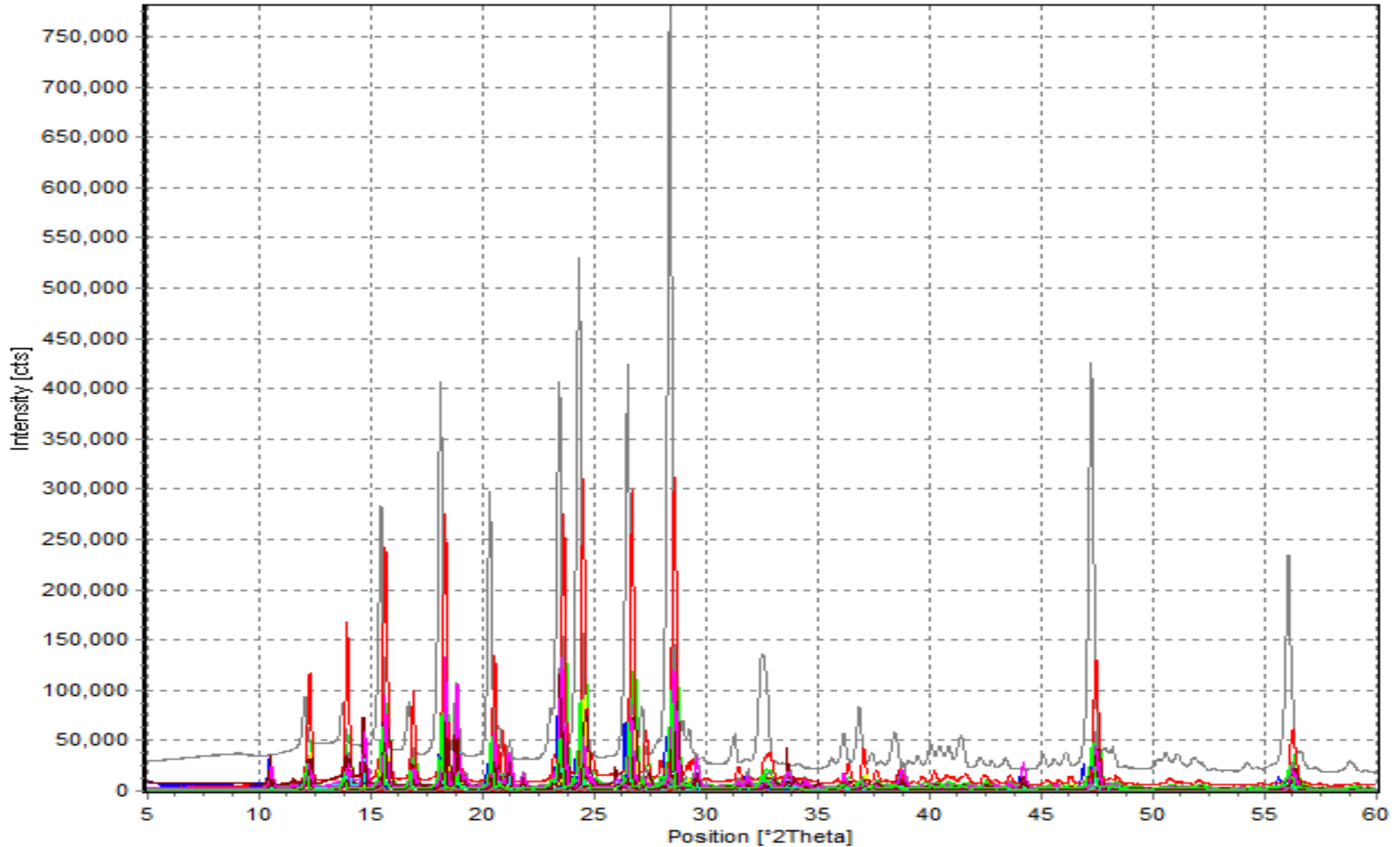
# PCA



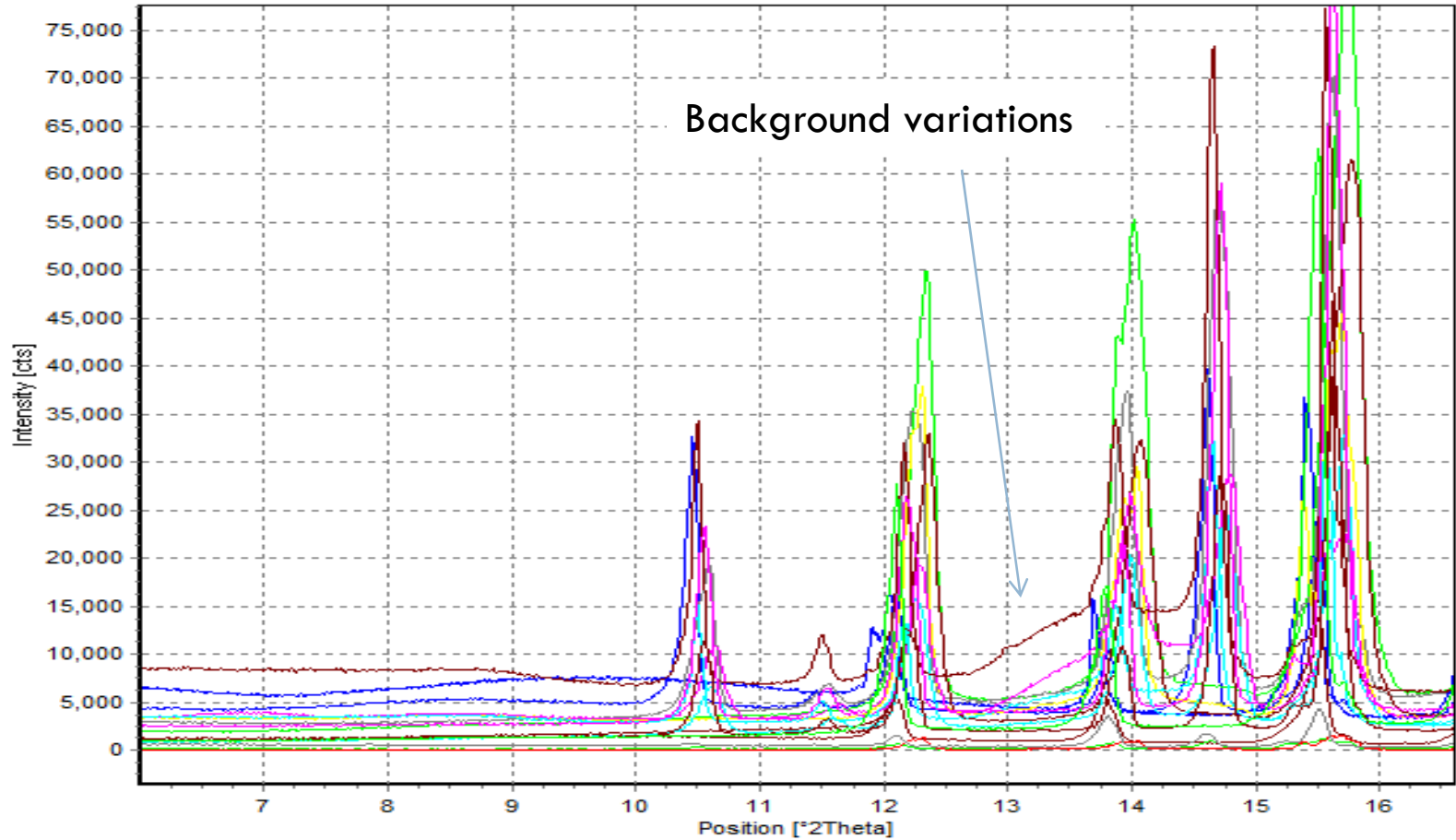
# Further clustering – after allowing pattern shifts



# Main cluster



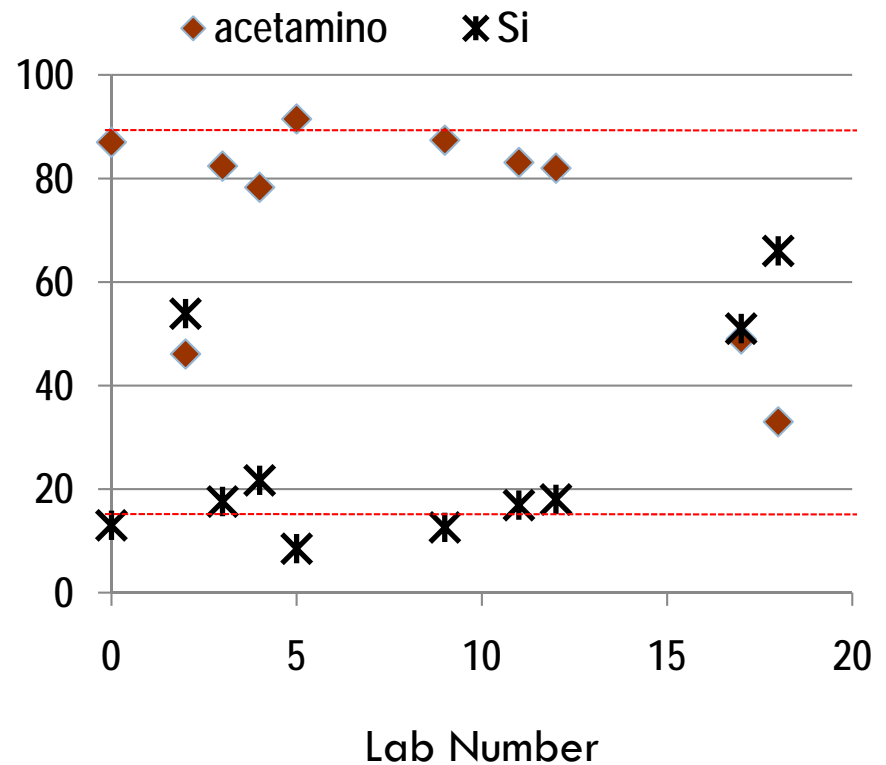
# Scaled Features



# Acetaminophen/Silicon

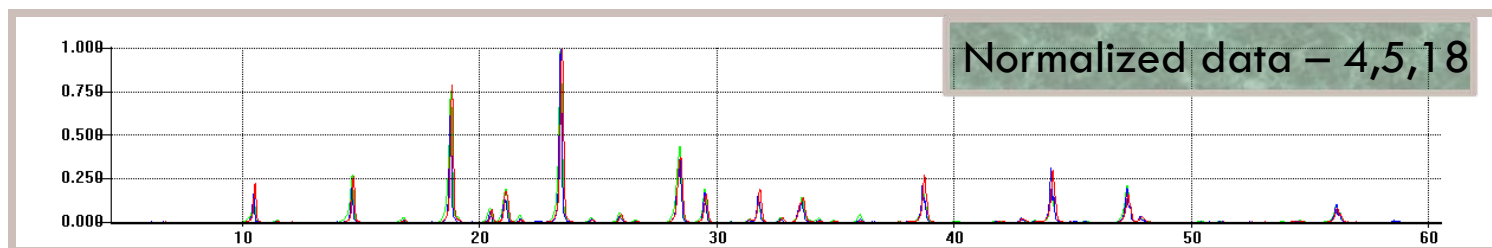
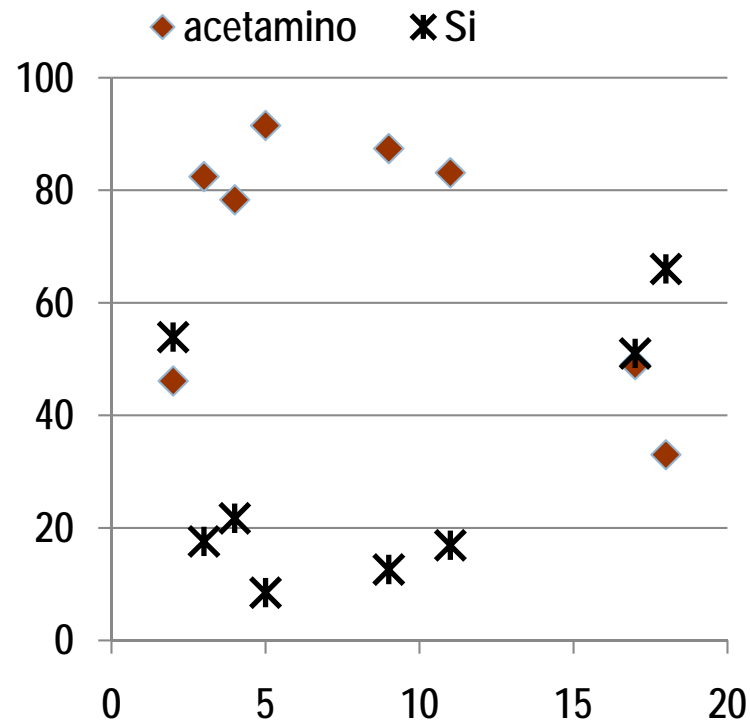
## - Tighest cluster

id	acetamino	silicon
0	87	13
2	46.1	53.9
3	82.4	17.6
4	78.3	21.7
5	91.5	8.5
9	87.4	12.6
11	83.1	16.9
12	82	18
17	49	51
18	33	66



# Acetaminophen/Silicon – 85/15

id	acetamino	silicon
2	46.1	53.9
3	82.416	17.584
4	78.3	21.7
5	91.5	8.5
9	87.4	12.6
11	83.1	16.9
17	49	51
18	33	66



# Acetaminophen/Silicon



Processing very similar data resulted in very different results

Were the correct polymorphs used ?

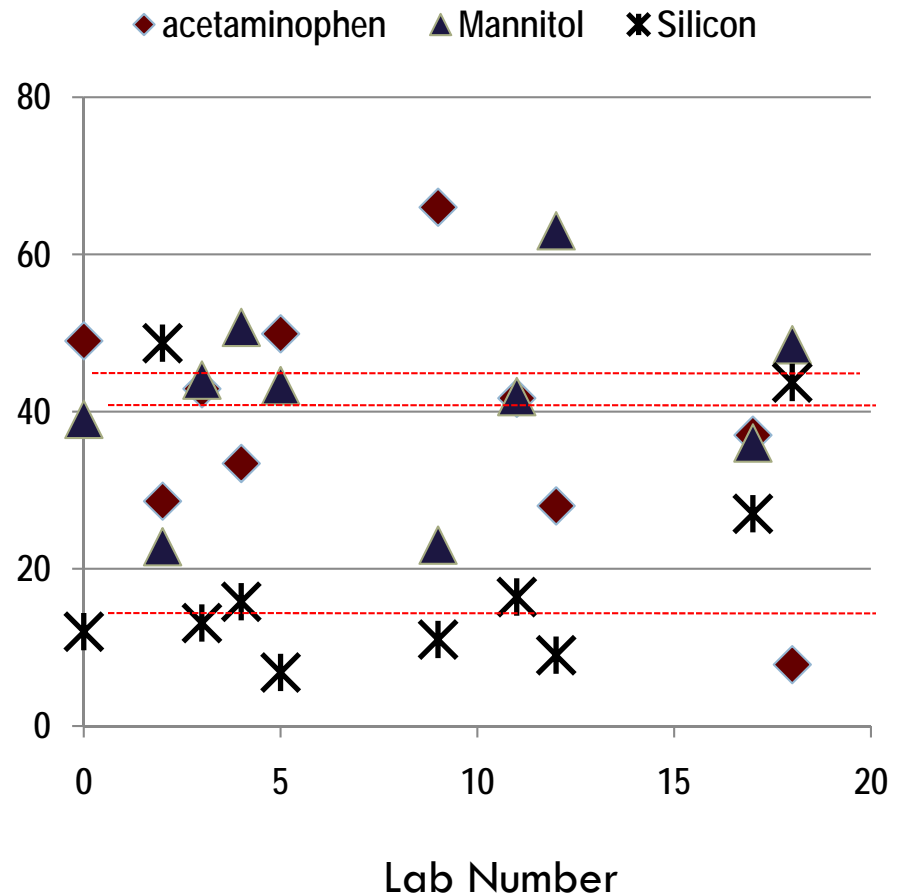
Can the program handle orientation ?

Were specimen displacements adjusted ?

# Acetaminophen/Mannitol/Silicon

id acetamino mannitol silicon

<b>0</b>	<b>49</b>	<b>39</b>	<b>12</b>
2	28.6	22.8	48.7
<b>3</b>	<b>42.9</b>	<b>44</b>	<b>13.1</b>
4	33.4	50.7	15.8
5	49.9	43.3	6.8
9	66	23	11
<b>11</b>	<b>41.7</b>	<b>41.9</b>	<b>16.4</b>
12	28	63	9
17	37	36	27
18	7.8	48.5	43.7



id acetamino mannitol silicon

2 28.6 22.8 48.7

3 42.85 44.01 13.14

4 33.4 50.7 15.8

5 49.9 43.3 6.8

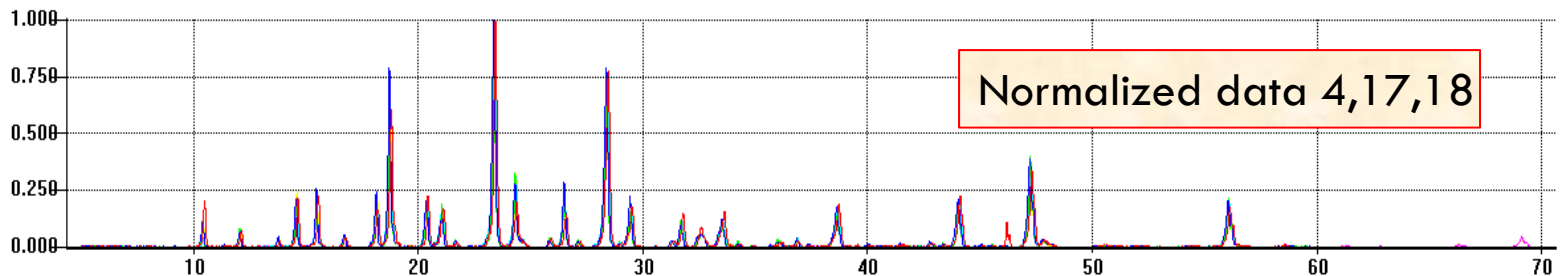
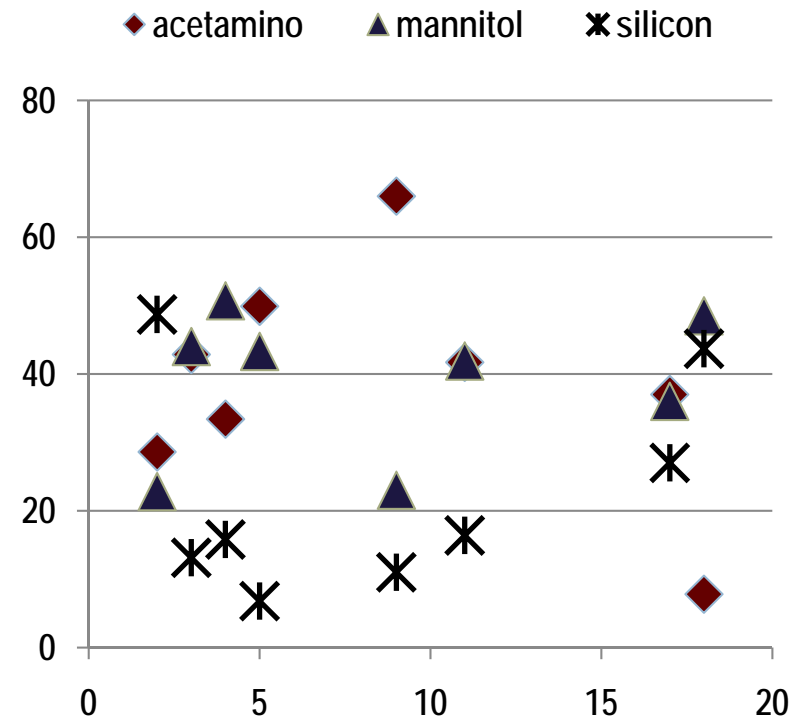
9 66 23 11

11 41.7 41.9 16.4

17 37 36 27

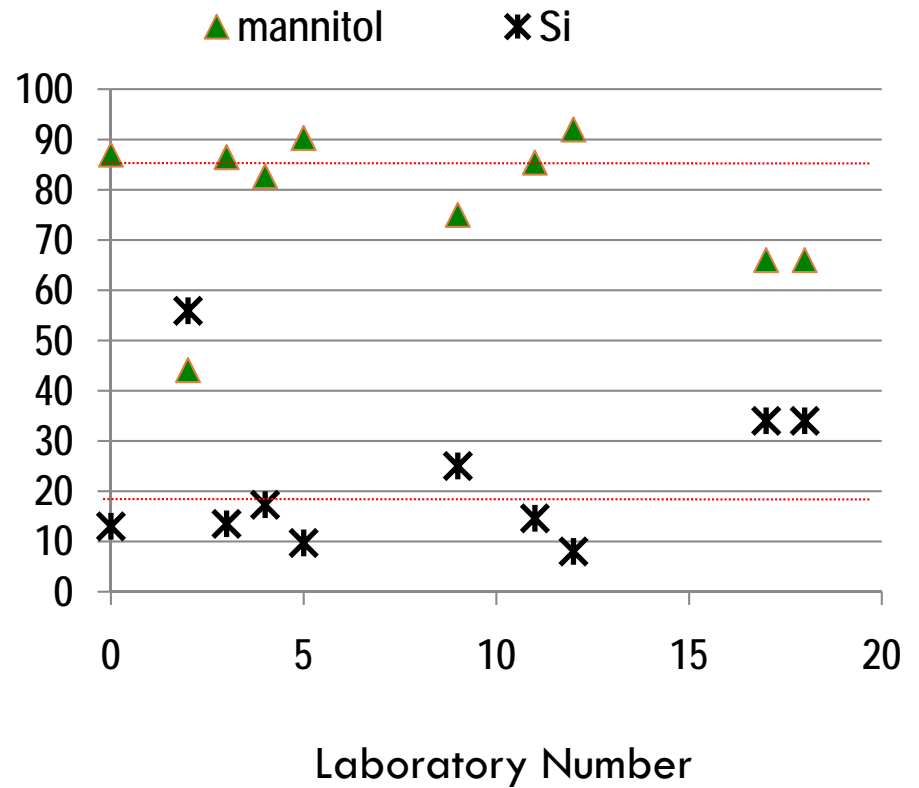
18 7.8 48.5 43.7

Acetaminophen  
/Mannitol/Silicon  
45/40/15



# Mannitol/Silicon

id	mannitol	silicon
0	87	13
2	44.1	55.9
3	86.5	13.5
4	82.7	17.3
5	90.3	9.7
9	75	25
11	85.4	14.6
12	92	8
17	66	34
18	66	34



id mannitol silicon

2 44.1 55.9

3 86.5 13.5

4 82.7 17.3

5 90.3 9.7

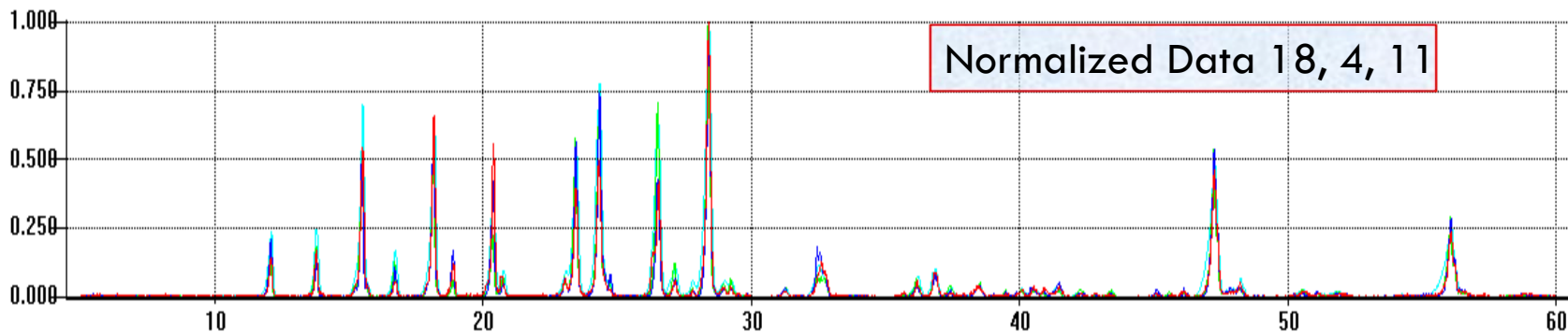
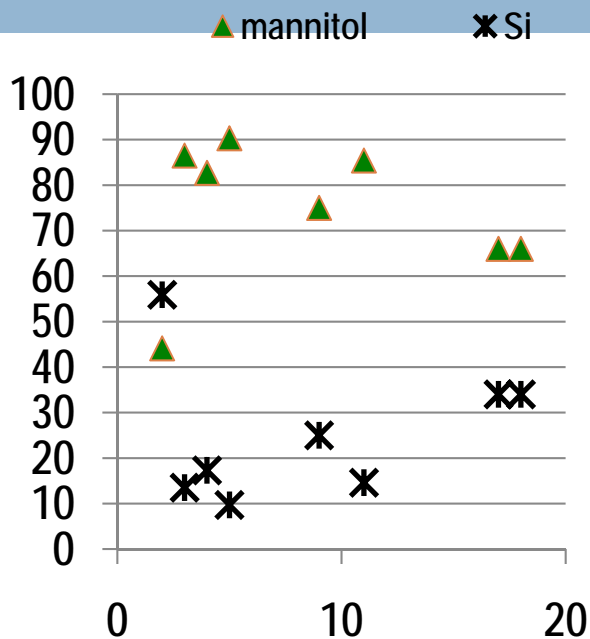
9 75 25

11 85.4 14.6

17 66 34

18 66 34

# Mannitol/Silicon 85/15



# Analysis



Laboratories 0, 3 and 11 achieved good results on all specimens  
Used cavity, capillary and foil mounts

Laboratories 2, 17 and 18 all overestimated Silicon concentration  
All 3 used cavity mounts  
They used 3 different analysis programs

Laboratory 18 had reproducible data that was very comparable to other laboratories on the same sample. This suggest data processing was the problem.

As a check Lab 17,18 data were refined at ICDD – and very different results were obtained.

# Scaling Factors – I/Ic

	<u>Best Value</u>	<u>Known range</u>	
Silicon	4.55	1-5	Polymorphic
Mannitol (beta-D)	0.51	0.48-0.66	Polymorphic
Acetaminophen (Form I)	0.63	0.5-1.03	Polymorphic

PDF #	QM ▲	Chemical Formula	Compound Name	I/Ic	Year
00-022-1793	S	C6 H14 O6	α-D-Mannitol		
00-022-1797	S	C6 H14 O6	β-D-Mannitol		
02-062-0119	S	C6 H14 O6	D-Mannitol	0.48	1968
02-069-8458	S	C6 H14 O6	D-Mannitol	0.51	1997
02-084-2598	S	C6 H14 O6	D-Mannitol	0.46	2003
02-084-2599	S	C6 H14 O6	D-Mannitol	0.51	2003
02-084-2600	S	C6 H14 O6	D-Mannitol	0.66	2003
00-008-0753	I	C6 H14 O6	D-Mannitol		1956
00-022-1794	I	C6 H14 O6	δ-D-Mannitol		
02-062-0075	I	C6 H14 O6	DL-Mannitol	0.65	1977
02-062-0118	B	C6 H14 O6	D-Mannitol	0.5	1968
00-047-2052	O	C6 H14 O6	Mannitol		1991

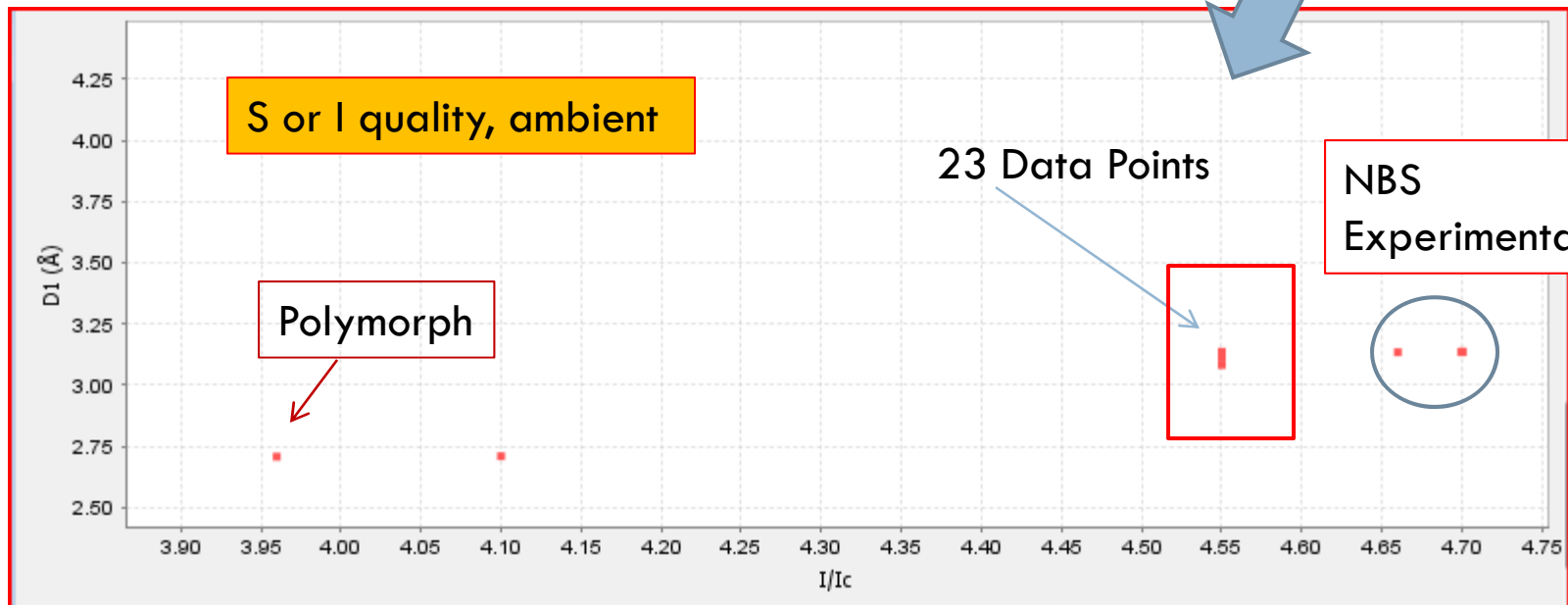
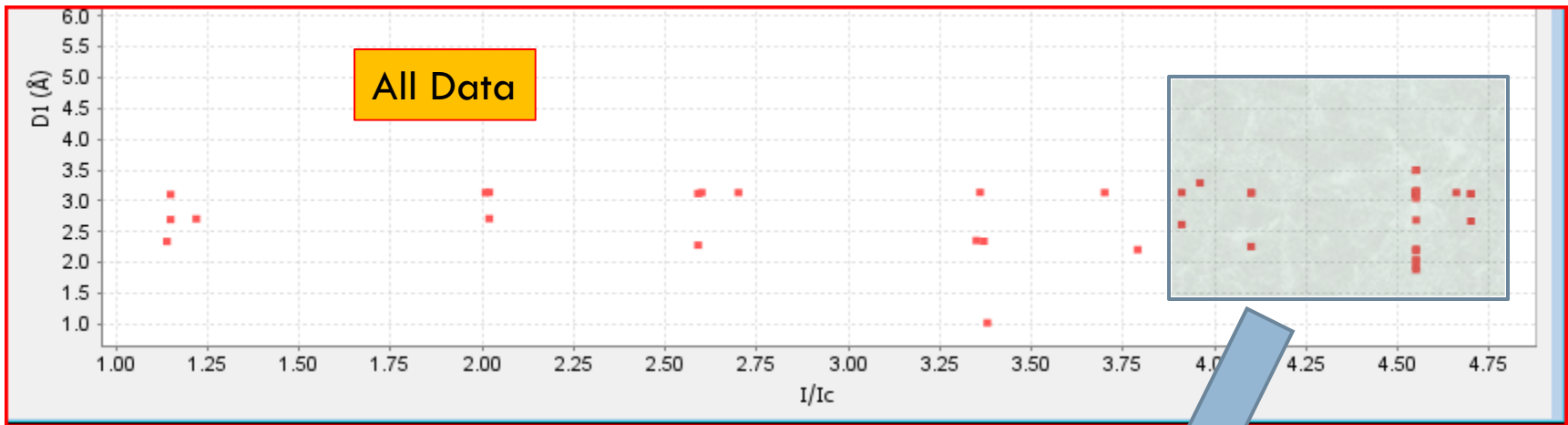
## Suggest

Let Search/Match pick  
The polymorph

Then use highest quality  
ambient data

# Selection of Reference Structures

## $I/I_c$ – Scale Factor for Silicon



# Observations

## **Specimen Prep**

Several specimens did not exhibit representative sampling

Orientation was observed

Specimen displacement was frequently observed

Granularity was observable from the acetaminophen data

In otherwords- all the well known factors that can cause poor results were present

## **Processing**

Each component has polymorphs – choosing the appropriate structure was critical (i.e. good search match identification)

Specimen prep error could lead to false identification among close choices between the polymorphs

The ability to adjust for orientation was very important

Were observed displacements or zero point shifts corrected ?

# Results

<u>Laboratory</u>	<u>Data Resolution</u>	<u>Intensity</u>	<u>Data Processing</u>	<u>Overall Results</u>
0	Good	Strong	Excellent	<u>Excellent</u>
2	No Raw Data			Poor
<b>3</b>	<b>Poor (grainy)</b>	<u>Med</u>	<u>Excellent</u>	<u>Excellent</u>
4	Excellent	Med	Good	Good
5	Good	Strong	Average	Average
9	Poor (bkgd)	Weak	Good	Average
<b>11</b>	<b>Moderate</b>	<u>Strong</u>	<u>Excellent</u>	<u>Excellent</u>
17	Good	Med	Poor	Poor
18	Excellent	Med	Poor	Poor
19	Excellent	Strong		

Poor to moderate resolution but reproducible strong intensity (i.e. good counting statistics)  
- produces excellent results

Excellent is ~ within 5 % absolute value