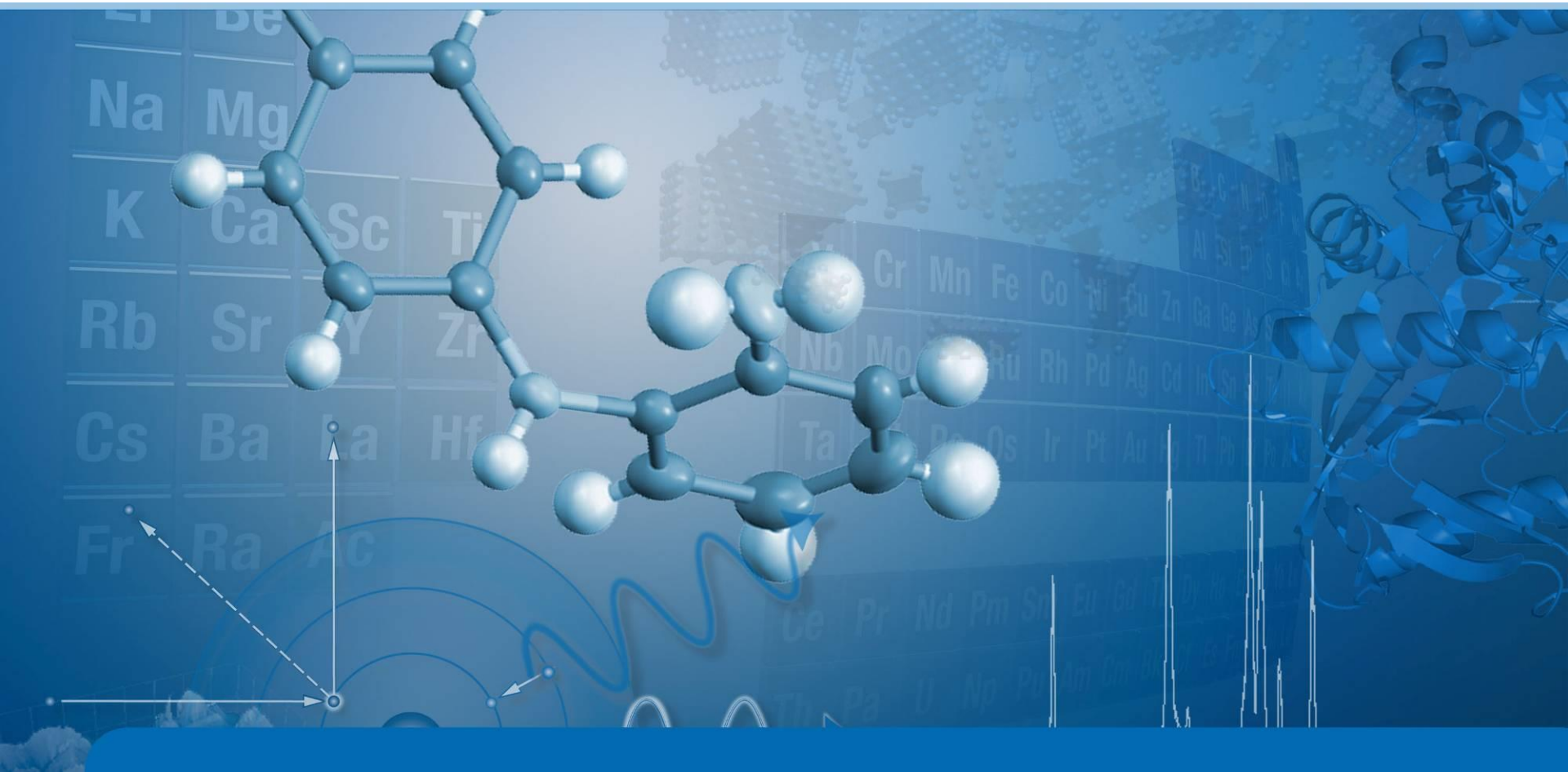
Issues in Quantitative Phase Analysis

Arnt Kern & Ian Madsen



This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

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Issues in Quantitative Phase Analysis

Limitations in accuracy and precision are mostly experimental

- Mathematical basis and methodology of quantitative phase analysis is well established and work OK
- Errors arise during application of methods ("PICNIC")

Sample related errors

- The material is not an "*ideal powder*"
  - Preferred orientation
  - Particle statistics
  - ...
- Absorption
- ...

Issues in Quantitative Phase Analysis

Operator errors

- Incomplete / wrong phase identification

The Reynolds Cup – what is needed to win?

Mark D Raven and Peter G Self

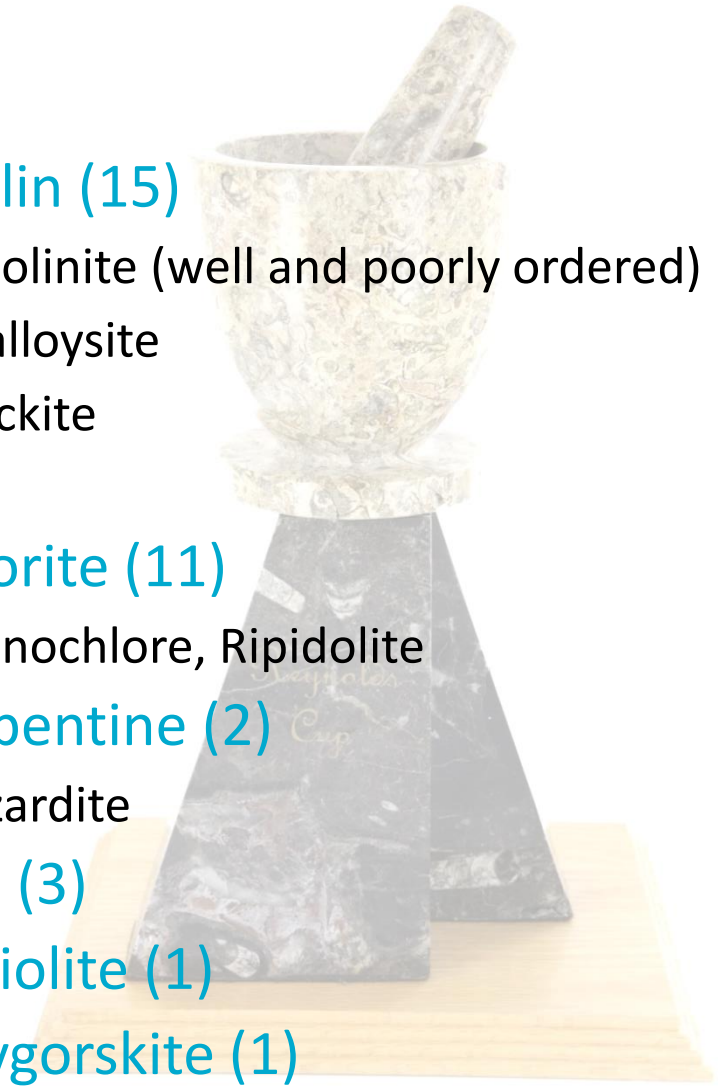
29 July 2014

Non clay minerals (2002-2012)

- Quartz (18)
- K-feldspar (13)
- Plagioclase (14)
- Calcite (12)
- Dolomite (10)
- Magnesite (4)
- Aragonite (3)
- Huntite (1)
- Halite (6)
- Pyrite (7)
- Siderite (8)
- Barite (5)
- Gypsum (2)
- Anhydrite (2)
- Alunite (1)
- Hematite (6)
- Goethite (5)
- Magnetite (4)
- Anatase (9)
- Rutile (3)
- Ilmenite (3)
- Gibbsite (3)
- Bohmite (1)
- Fluorite (2)
- Apatite (1)
- Tourmaline (2)
- Zircon (2)
- Spinel (1)
- Opal-CT (1)
- Amphibole (3)
- Zeolite (1)
- Epidote (1)
- Birnessite (1)
- Arcanite (1)
- Amorphous (6)

Clay minerals (2002-2012)

- 2:1 Dioctahedral Clays (18)
  - Smectite (montmorillonite, nontronite)
  - Mixed layered (illite-smectite, glauconite-smectite)
  - Mica/Illite (muscovite $2M_1$, illite $1M_d$, 1M)
- 2:1 Trioctahedral Clays (6)
  - Smectite (saponite)
  - Vermiculite
  - Mixed layered (corrensite)
  - Mica (biotite)
- Kaolin (15)
  - Kaolinite (well and poorly ordered)
  - Halloysite
  - Dickite
- Chlorite (11)
  - Clinochlore, Ripidolite
- Serpentine (2)
  - Lizardite
- Talc (3)
- Sepiolite (1)
- Palygorskite (1)



Misidentified phases (2002-2012)

- Actinolite
- Aegerine
- Aerinite
- Akaganeite
- Albite/anorthite
- Allophane
- Alluaudite
- Almandine
- Al-Mg
- AlO
- Alumina gamma
- Aluminite
- Alunite
- Alunogen
- Amorphous
- Amorphous (Allophane)
- Amorphous KAlSi3O8
- Amorphous Si
- Amorphous SiO2
- Amorphous Volcanic Glass
- Amphibole
- Analcime
- Anatase
- Andesine
- Anhydrite
- Ankerite
- Anorthite
- Antigorite
- Antlerite
- Apatite
- Aragonite
- Arcanite
- Arsenolite As2O3
- Augite
- Barite
- Bazalt
- Berthierine
- Biotite
- Birnessite
- Bromcarnallite
- Brookite
- Brucite
- Brushite
- Bytownite
- C6H5O3PZn
- Calcite
- CaMg2Al16O27
- Carbonate-fluorapatite
- Carnallite
- CaSiO3
- Celestine
- Chabazite
- Chalcosite
- Chlorargyrite
- Chlorite Dioctahe
- Chlorite Trioctahe
- Chlorite-Montmo
- Chlorite-Smectite
- Chlorite-Vermiculi
- Chromite
- Chrysotile
- Clinochlore
- Clinoenstate
- Clinoptilolite
- ClinoPyroxene
- Clinozoisite
- Cordierite
- Corrensite
- Corundum
- Cotunnite
- Cristobalite
- Cryptohalite
- Crysotile
- Diaspore
- Dickite
- Dickite/Nacrite
- Diopside
- Dolomite
- Dolomite/Ankerite
- Elpidite
- Enstatite
- Epidote
- Euclase
- Faujasite
- Fe oxide
- Fedorite
- par (Kspar)
- ydrite
- e magnesian
- apatite
- erite
- ite
- Garnet
- Gehlenite
- Gibbsite
- Gismondine
- Glass/Obsidian
- Glauberite
- Glauconite
- e
- otassian
- te
- Hedenbergite
- Hematite
- Hercynite
- Heulandite
- Hexahydrite
- Hornblende
- Hotsonite
- Hyalophane
- hydrated Ca-Mg carbonate
- ydrocalumite
- ydrotalcite
- ydroxyapophyllite
- ydroxylapatite
- persthene
- ite Tri
- Ilmenite
- ilterstratified (t
- Iron
- Iron Silicon
- Jarosite
- KAlSiO4
- Kaolinite
- kaolinite/smectite
- Kaolinite-Chlorite
- K-feldspar
- Kieserite
- K-rich Chlorite
- Kutnohorite
- Laueite
- Laumonite
- Lepidocrocite
- Leucite
- Lime
- Lithosite
- Lizardite
- Magnesioferrite
- Magnesite
- Magnetite
- Malachite
- Manganite
- Melantenite
- Mg7Zn3
- Mg-calcite
- MgSO4
- Mica
- Mica Trioctahedral
- Mica-Vermiculite Trioctahedral
- Microcline
- Missing
- Monazite
- Monohydrocalcite
- Montmorillonite (Tri)
- Moschellandsbergite
- Mullite
- Nacrite
- Na-Feldspar
- Natrolite
- Nepheline
- Nitride Silicon
- Nordstrandite
- Norrishite
- Oligoclase
- Olivine
- Opal
- Opal CT
- Orthoclase
- OrthoPyroxene
- Osumilite
- Others not precisely identified
- oxide 1
- oxide 2
- Palygorskite
- Periclase
- Perovskite
- Phillipsite
- Phlogopite (2M1)
- Phlogopite (mica-trioctahedral)
- phosphate hydrate
- Plagioclase
- Portlandite
- Potarite
- Prehnite
- Pseudobrookite
- Pumpellyite
- Pyrite
- Pyrolusite
- pyrophyllite 1T
- pyrophyllite 2M
- Pyroxene
- Pyroxene (Augite)
- Pyroxene (Ferroan Diopside)
- Pyrrhotite
- Rectorite
- Reyerite
- Rhodochrosite
- Rhodonite
- Rodolicoite
- Rutile
- Sanidine
- ite
- nite
- ite
- Serpentine
- Siderite
- Siderite (Mn-rich)
- Siderite(not Mg)
- Silicon
- Silicon dioxide
- Sillimanite
- Smectite trioctahedral
- Smithsonite
- Sodalite
- Spencerite
- Sphalerite iron
- Spinel
- olite
- tianite
- e
- nite
- olnokite
- Talc
- Thenardite
- Thermonatrite
- Titanite
- Titanomagnetite
- Tobermorite
- Tourmaline
- Trimerite
- Trydymite
- Tungstite
- Unidentified
- Unnamed hydrate
- Vaterite
- Vauxite
- Vermiculite
- Vermiculite Trioctahedral
- Vermiculite/illite
- Vermiculite-Smectite Trioctahedral
- Vesuvianite
- Wagnerite
- Wavellite
- Whitlockite
- Whitmoreite
- Wollastonite
- Wroewolfeite
- Wuestite
- Zeolite
- Zeophyllite
- Zinnwaldite
- Zircon
- Zirconium sulphate hydroxide hydrate
- Zoisite

Al-Mg

AlO

As2O3

C6H5O3PZn

Chromite

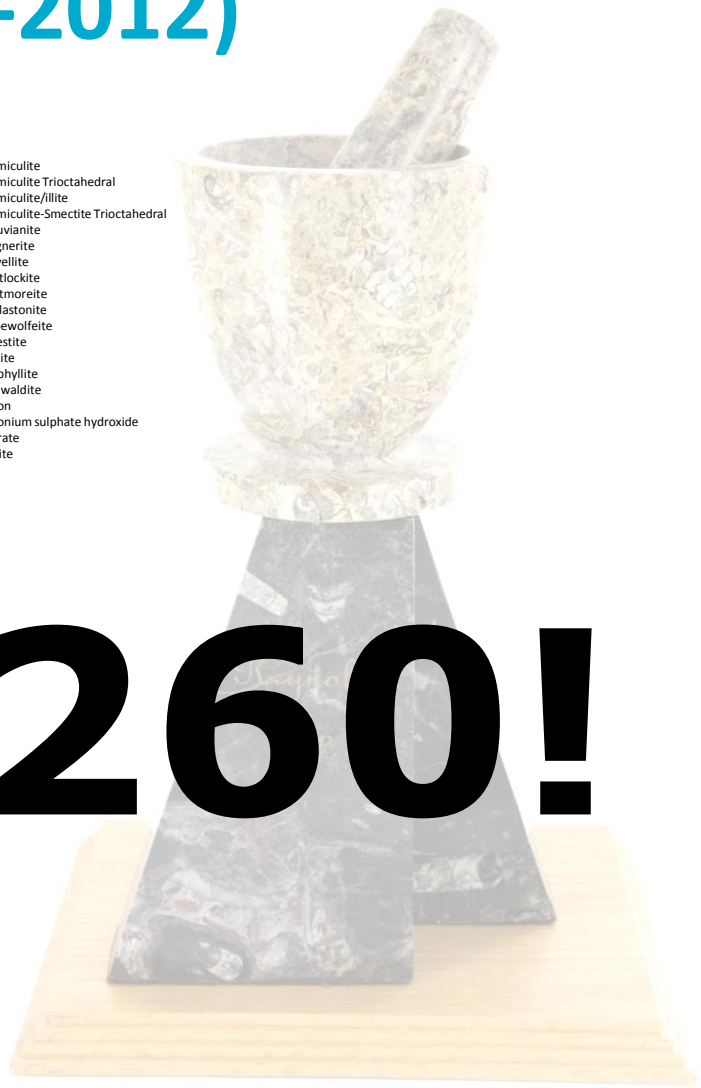
Iron

Mg7Zn3

Silicon

Nitride Silicon

260!



Issues in Quantitative Phase Analysis

Operator errors

- Incomplete / wrong phase identification
- Incorrect crystal structures: space group, atom coordinates, occupancy factors, temperature factors
- Use of poor profile / background models
- Failure to refine parameters: Unit cell, profile parameters, ...
- Refinement of parameters which are not supported by the data: Background, atom coordinates, occupancy factors, temperature factors, microstructure, ...

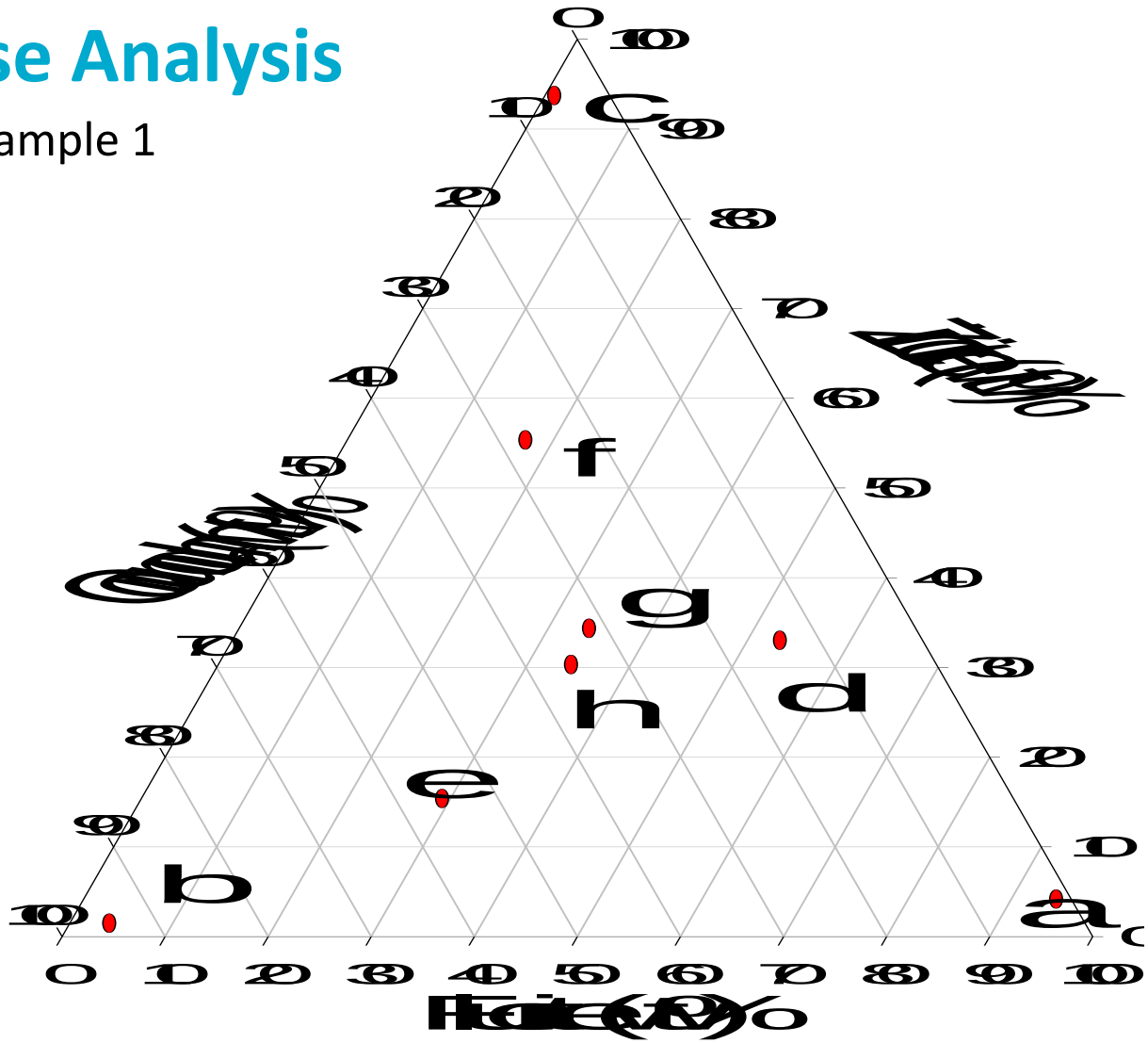
Issues in Quantitative Phase Analysis

Operator errors, ctd.

- Inappropriate use of correction models –
  just because you CAN doesn't mean you SHOULD!
  - Preferred orientation correction
  - Absorption correction
  - Non-constant diffraction volume
  - ...
- Acceptance of physically unrealistic parameters (esp. thermal parameters)
- Acceptance of incomplete refinements
  - High values of R-factors
  - Refined parameters not checked
  - Visual fit of model not checked

IUCr CPD Round Robin on Quantitative Phase Analysis

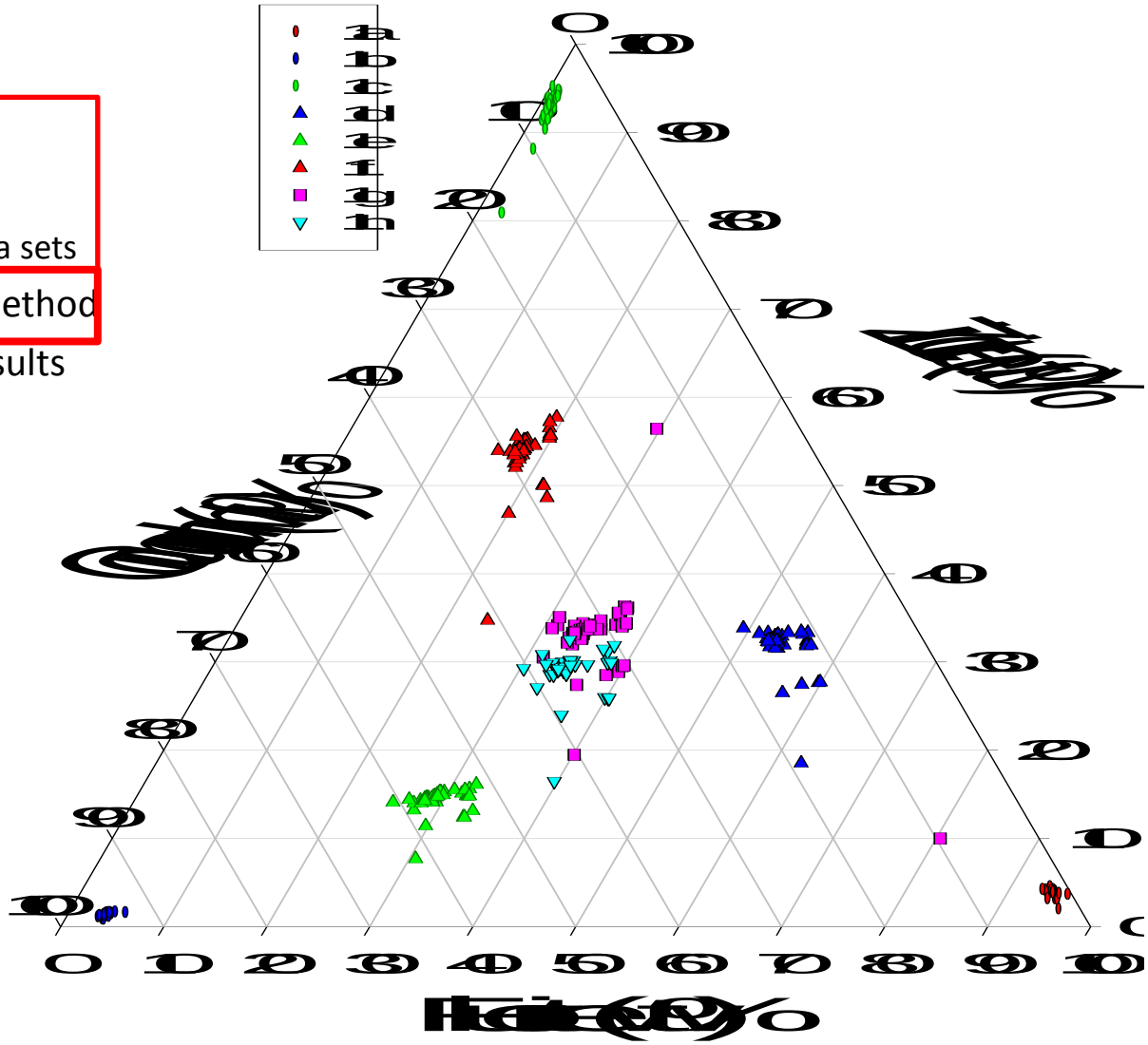
- Experimental design for Sample 1
  - Eight mixtures of 3 phases
    - Corundum – α-Al_2O_3
    - Fluorite – CaF_2
    - Zincite – ZnO
  - Each phase present at a range of concentrations
  - ~ 1.5, 5, 15, 30, 55, 95 wt%
- 'Simple' system
  - Well defined phases
  - Minimal peak overlap
  - Little absorption contrast



IUCr CPD Round Robin on QPA

CPD Supplied Data

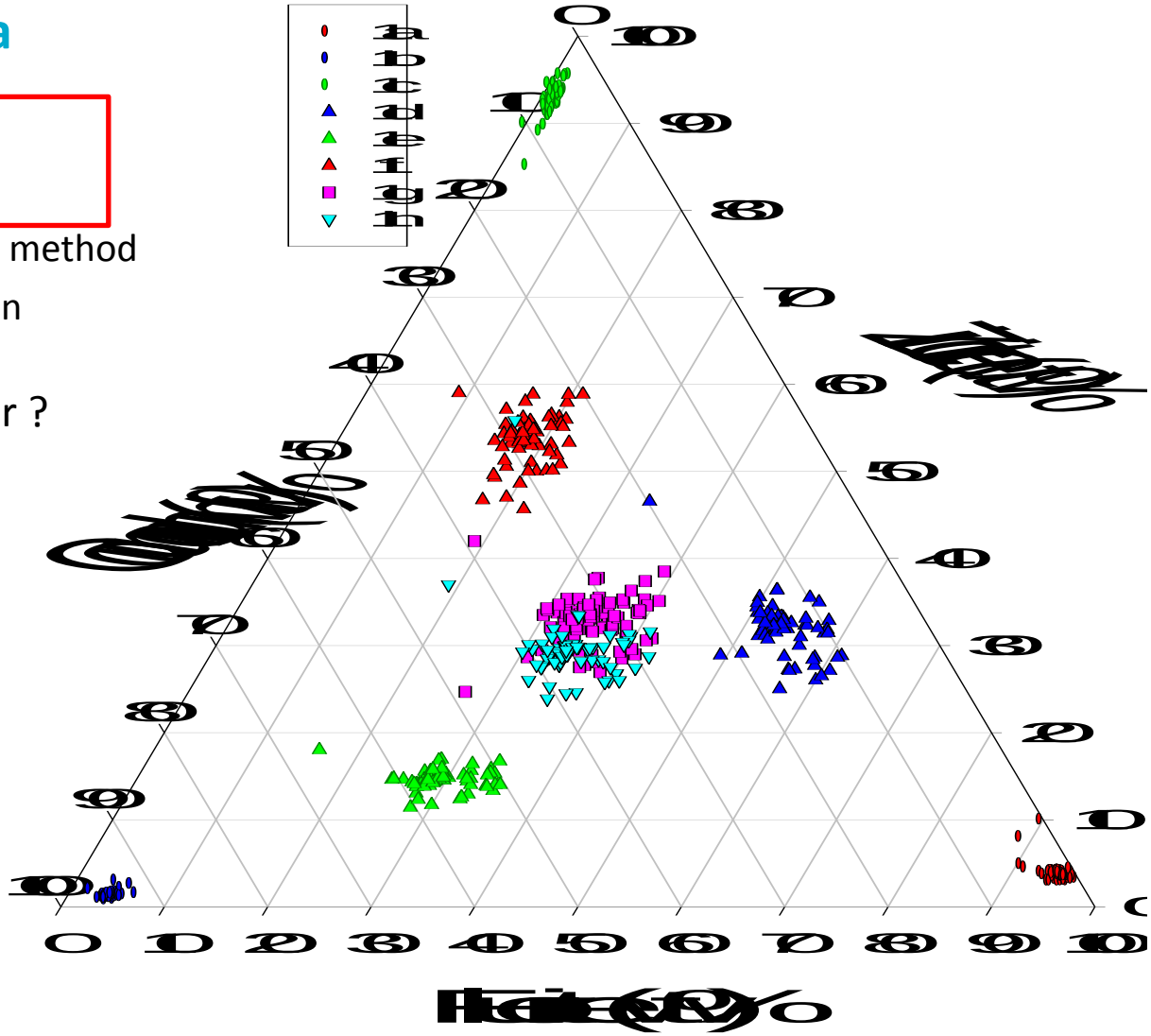
- Participant's results
  - CPD-supplied data
    - Everyone analysed the same data sets
  - 92% of returns used Rietveld method
  - Note considerable spread in results



IUCr CPD Round Robin on QPA

Participant Collected Data

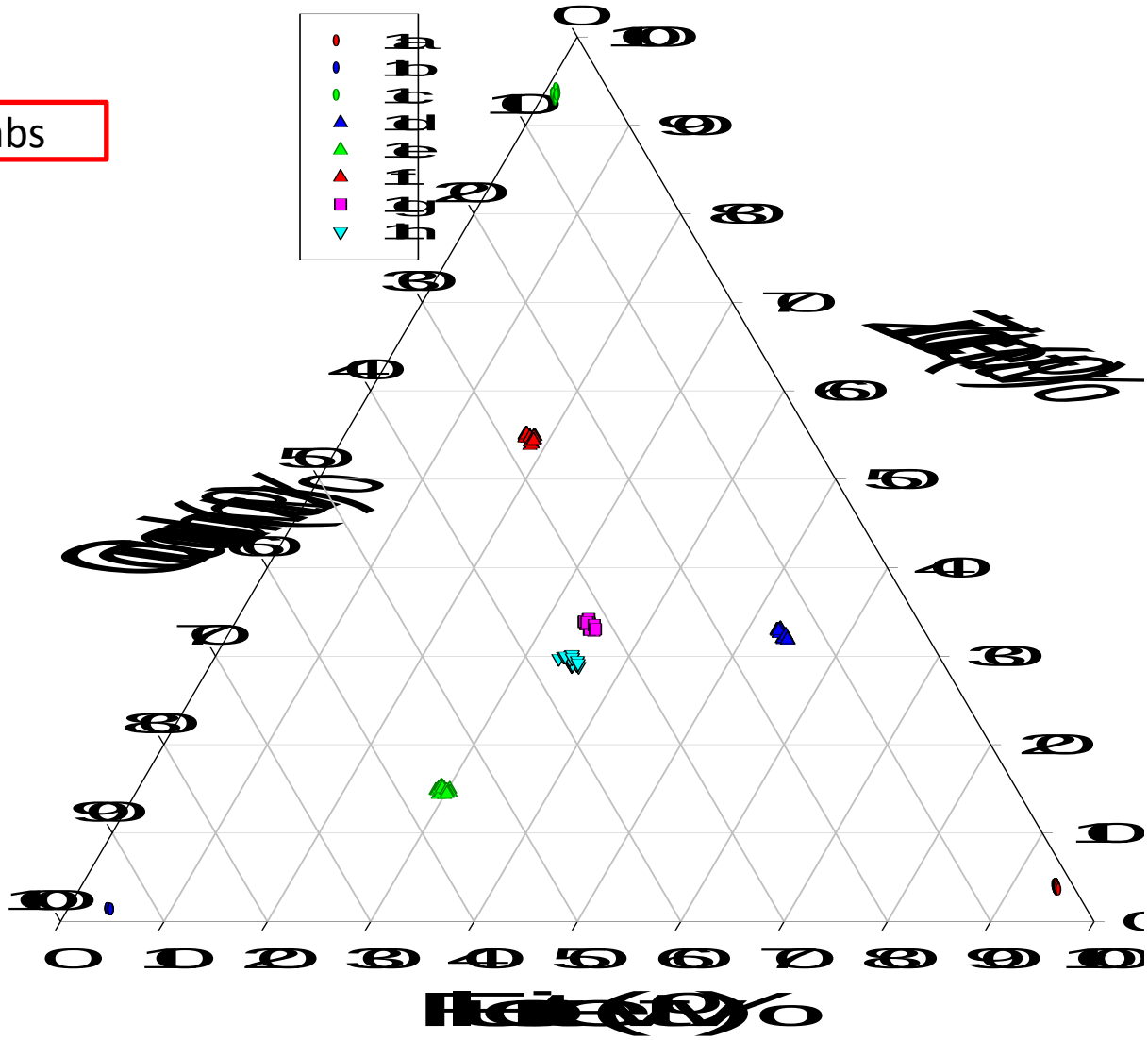
- Participant's results
  - Participant collected data
  - 75% of returns used a Rietveld method
  - Spread of results is greater than for the CPD-supplied data
- What are the sources of error ?
  - Methods ?
  - Sample preparation ?
  - Data collection ?
  - Data analysis ?



IUCr CPD Round Robin on QPA

Test of Various Methods

- Samples analysed in CSIRO labs
  - 3x replicates of 8 mixtures
- A range of methods used
  - 2x Rietveld packages
  - 2x Single Peak methods
  - 2x Iterative Least Squares
  - 1x Mean Normalised Intensity
  - XRF
- Summary
  - Methods work OK
  - Errors arise during application of methods



Sources of Errors

The sample - is it an *ideal powder*?

Preferred orientation

Particle statistics

Crystal structure data

Sources of Errors
The Sample - is it a *Ideal Powder*?

- *Powder*: A "solid containing small crystallites or particles that will flow when agitated", or similar, in accordance to the usual sense of the word in colloquial speech

Sources of Errors
The Sample - is it a *Ideal Powder*?

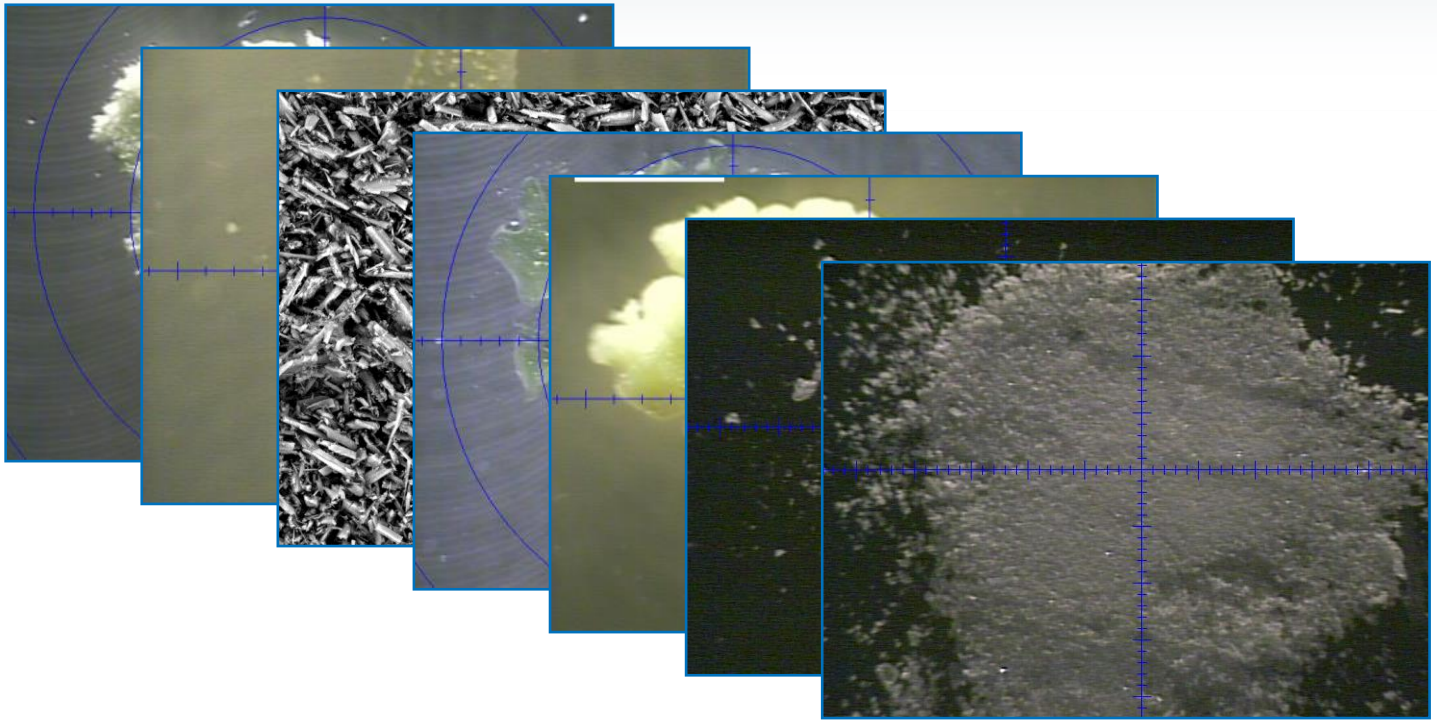
- ~~*Powder*: A "solid containing small crystallites or particles that will flow when agitated", or similar, in accordance to the usual sense of the word in colloquial speech~~

- *Powder*: A "large number of crystallites and/or particles (i.e. grains, agglomerates or aggregates; crystalline or non-crystalline) irrespective of any adhesion between them" and thus can be a loose powder (in the sense of common language), a solid block, a thin film or even a liquid" *

- *Ideal powder:* A "virtually unlimited number of sufficiently sized, randomly orientated, and spherical crystallites" *

* EN-1330-11 (2007)

Sources of Errors
The Sample - is it a *Ideal Powder*?

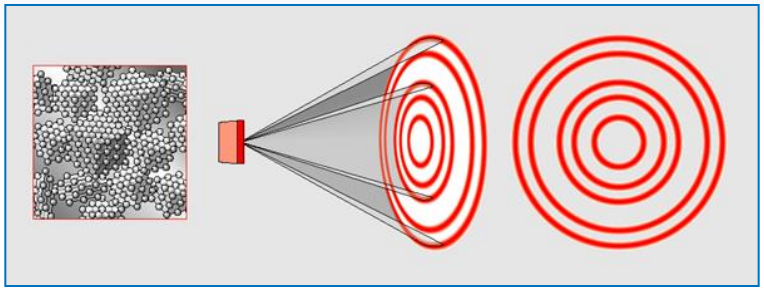


- None of these examples represents an *ideal powder*
- Sample preparation and presentation requires particular consideration

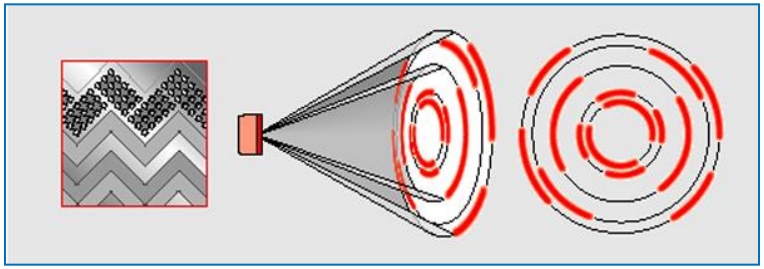
Sources of Errors

The sample - is it an *ideal powder*?
Preferred orientation
Particle statistics
Crystal structure data

Sources of Error
Preferred Orientation



Diffraction of an ideal powder

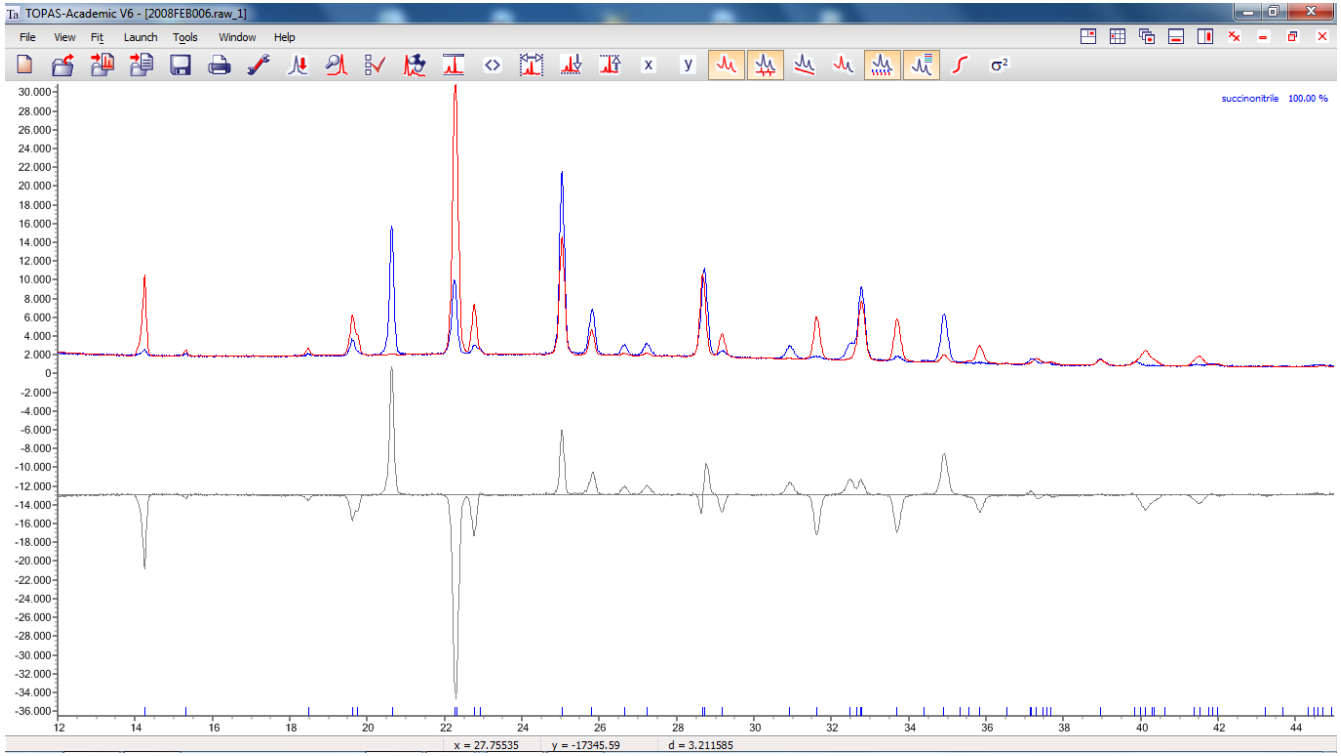


Diffraction of materials with preferred orientation

Sources of Error
Preferred Orientation

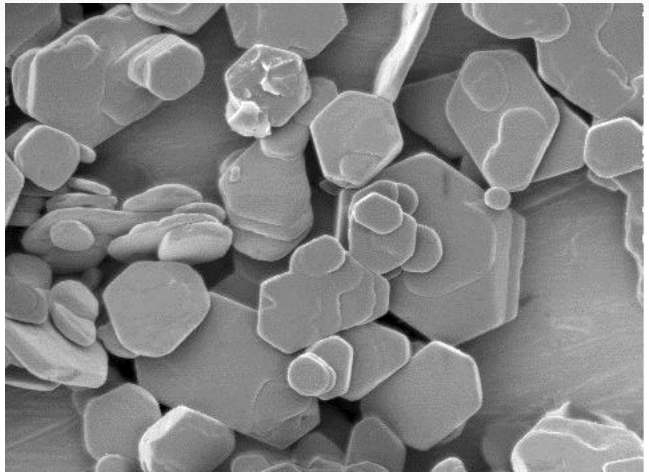
Example:

- Blue: Preferred orientation
- Red: No preferred orientation



Sources of Error
Preferred Orientation

- Most often seen in samples that contain crystallites with a platey or needle-like morphology
- Extent of orientation can depend greatly on how the sample is mounted

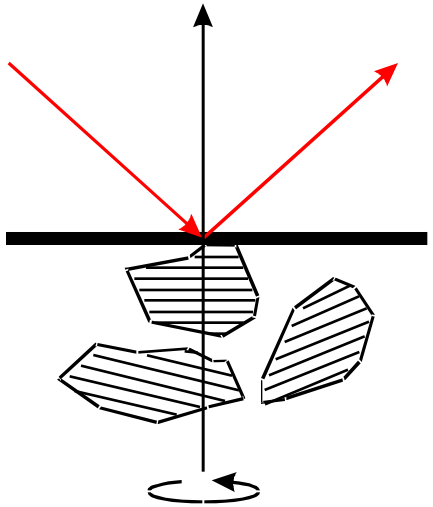


Remedy?

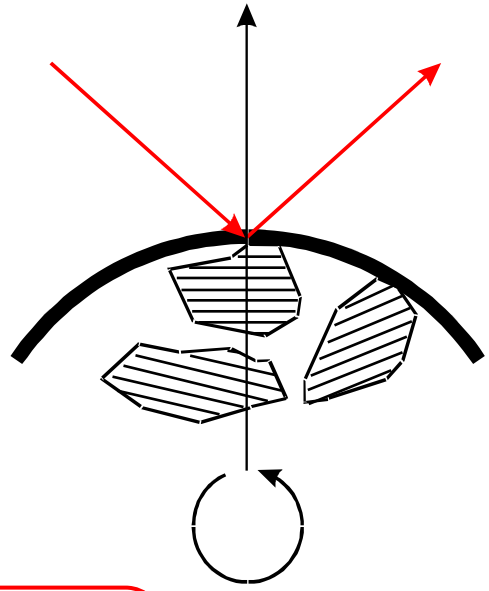
- Avoid software corrections
- Try to improve sample preparation (e.g. backloading) and / or presentation (transmission)
- Try to grind the sample
  - Do not destroy the sample (amorphization, phase transitions, ...)
  - Try different grinding techniques and perform grinding series to verify

Sources of Error
Preferred Orientation

- Bragg-Brentano geometry



- Parallel or focusing beam Debye-Scherrer geometry using capillaries

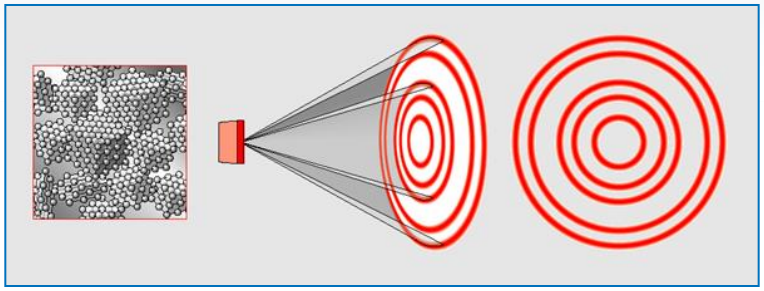


Rotation parallel to the scattering vector does not minimize preferred orientation effects!

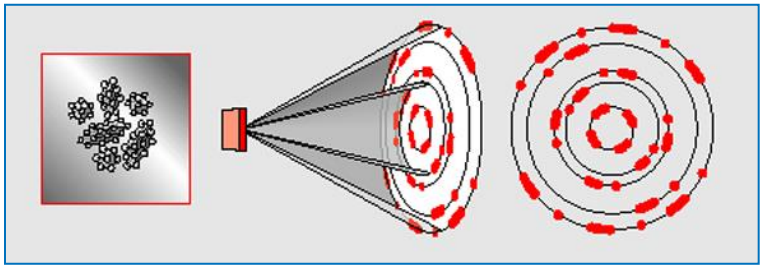
Sources of Errors

The sample - is it an *ideal powder*?
Preferred orientation
Particle statistics
Crystal structure data

Sources of Error
Particle Statistics

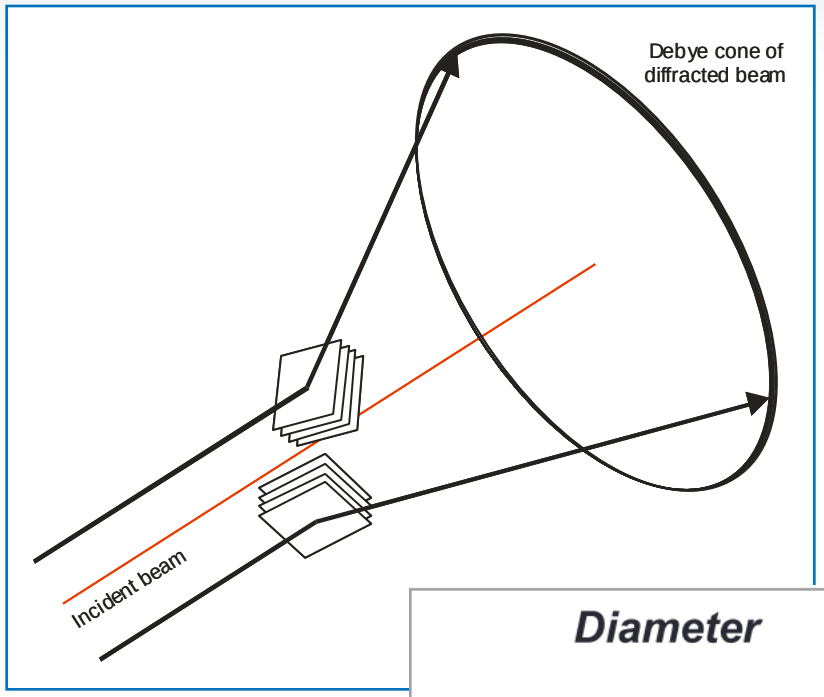


Diffraction of an ideal powder



Diffraction of a small number of crystallites ("spotiness effect")

Sources of Error
Particle Statistics



- Ideally some 10^8 - 10^{10} crystallites in the beam
- Ideally completely random orientation

Adapted from
S. Misture, 2002

Diameter	40µm	10µm	1µm
Crystallites / 20mm³	5.97×10^5	3.82×10^7	3.82×10^{10}
No. of diffracting crystallites	12	760	38000

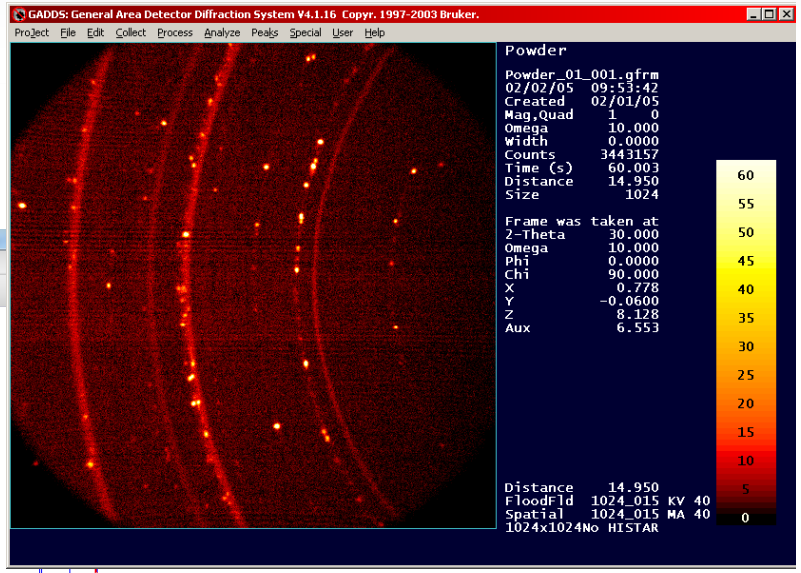
Sources of Error
Particle Statistics

- Sample contains large crystallite(s)
  - A single particle can cause problems
  - Larger particles have a stronger tendency to preferred orientation
- Too small number of crystallites
  - Sample only consists of a few crystallites or irradiated sample volume too small (⇨ micro-diffraction)
  - Parallel beam geometry: Large irradiated sample volume but too few crystallites diffract

Sources of Error
Preferred Orientation

Example:

- Blue: Particle statistics
- Red: No particle statistics

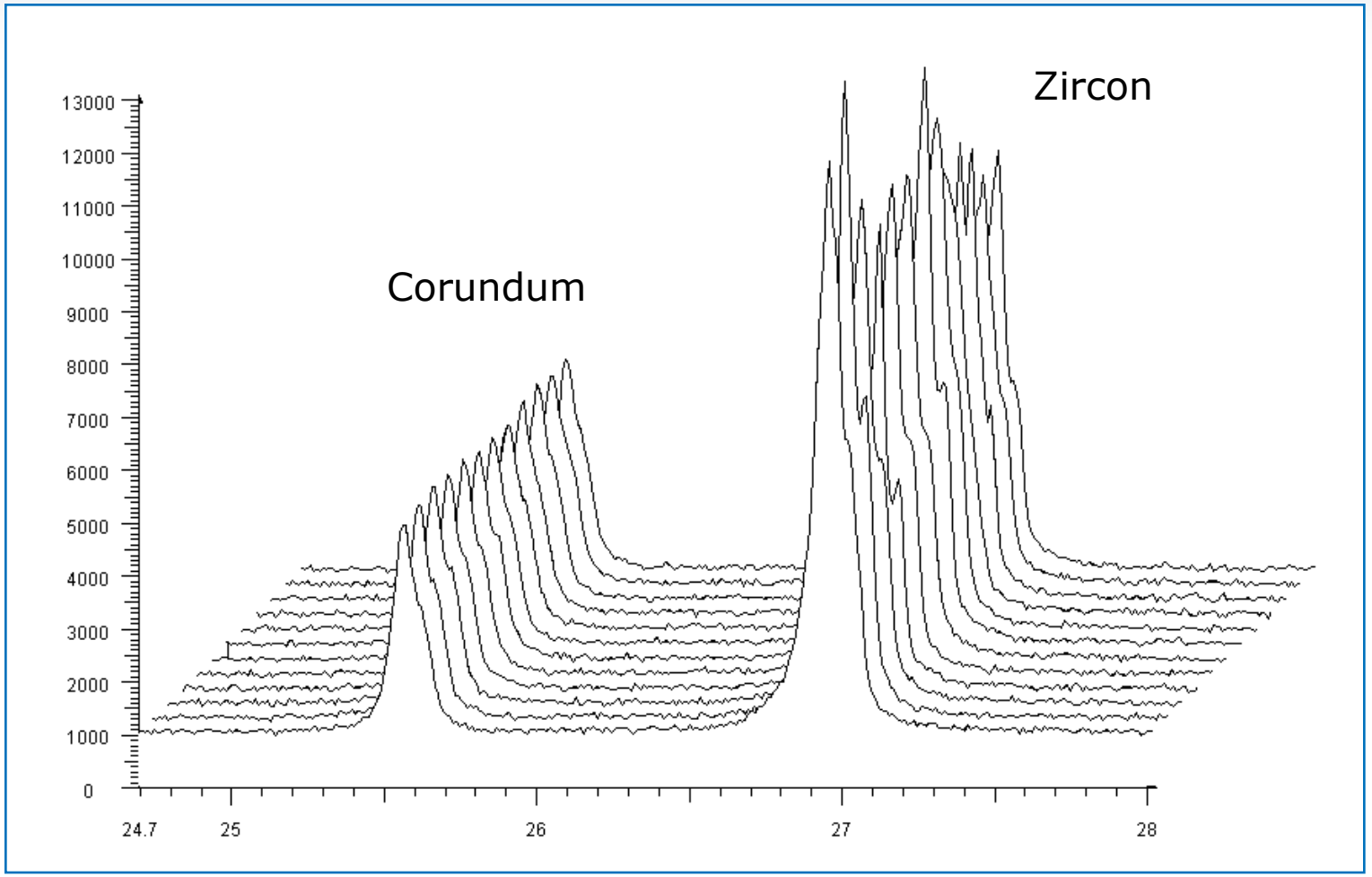


Sources of Error
Particle Statistics

Remedy?

- Spotiness effects cannot be corrected by software
  - Spotiness and preferred orientation effects are often confused
- Try to grind the sample
  - Do not destroy the sample (amorphization, phase transitions, ...)
  - Try different grinding techniques and perform grinding series to verify
- If no 2D detector system is available, indexed Phi-scans can help to detect spotiness effects

CPD-4
Phi Scans, 30° Steps



Sources of Errors

The sample - is it an *ideal powder*?
Preferred orientation
Particle statistics
Crystal structure data

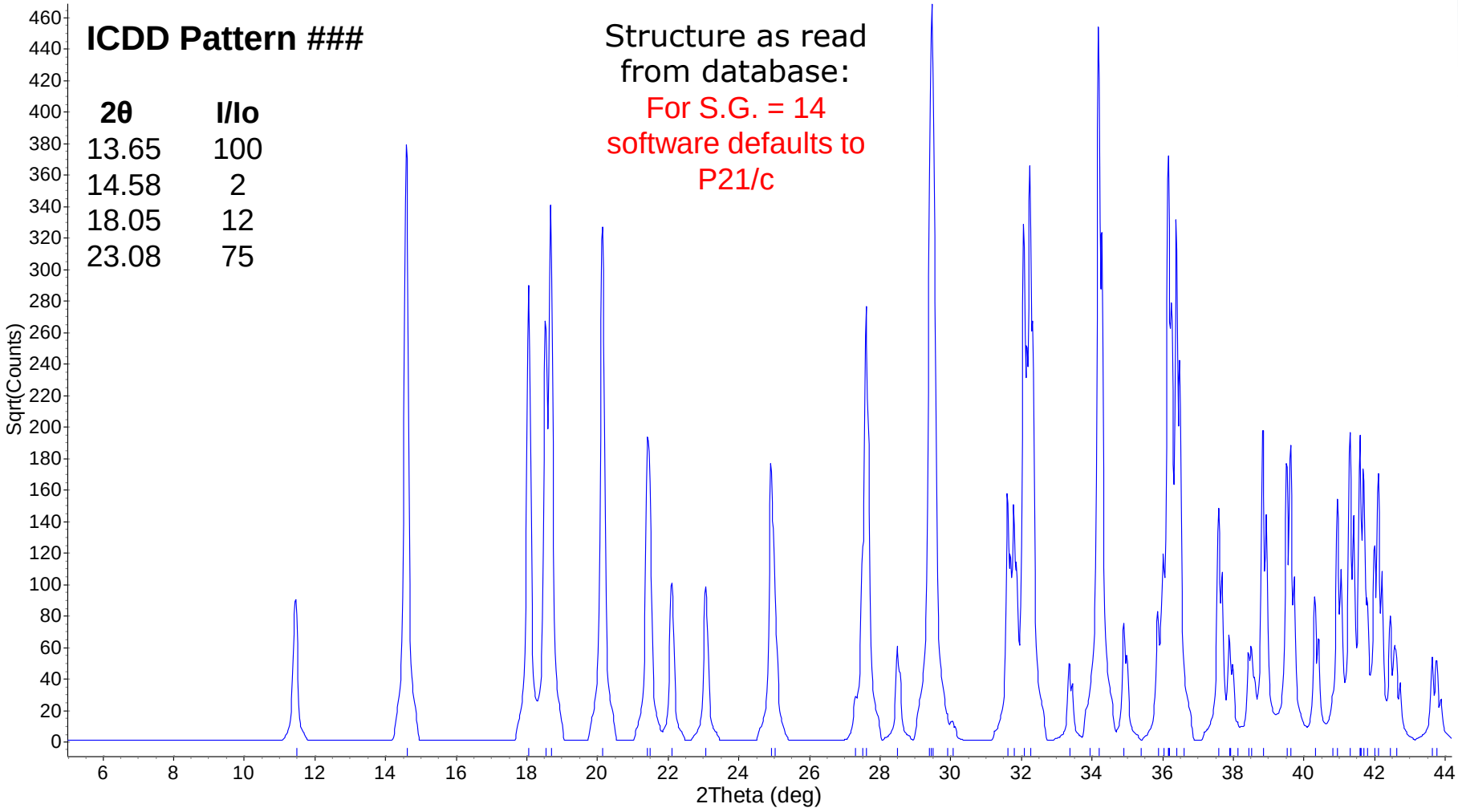
XYZ.3H_2O – Calculated Pattern

⇨ Structure as read from database

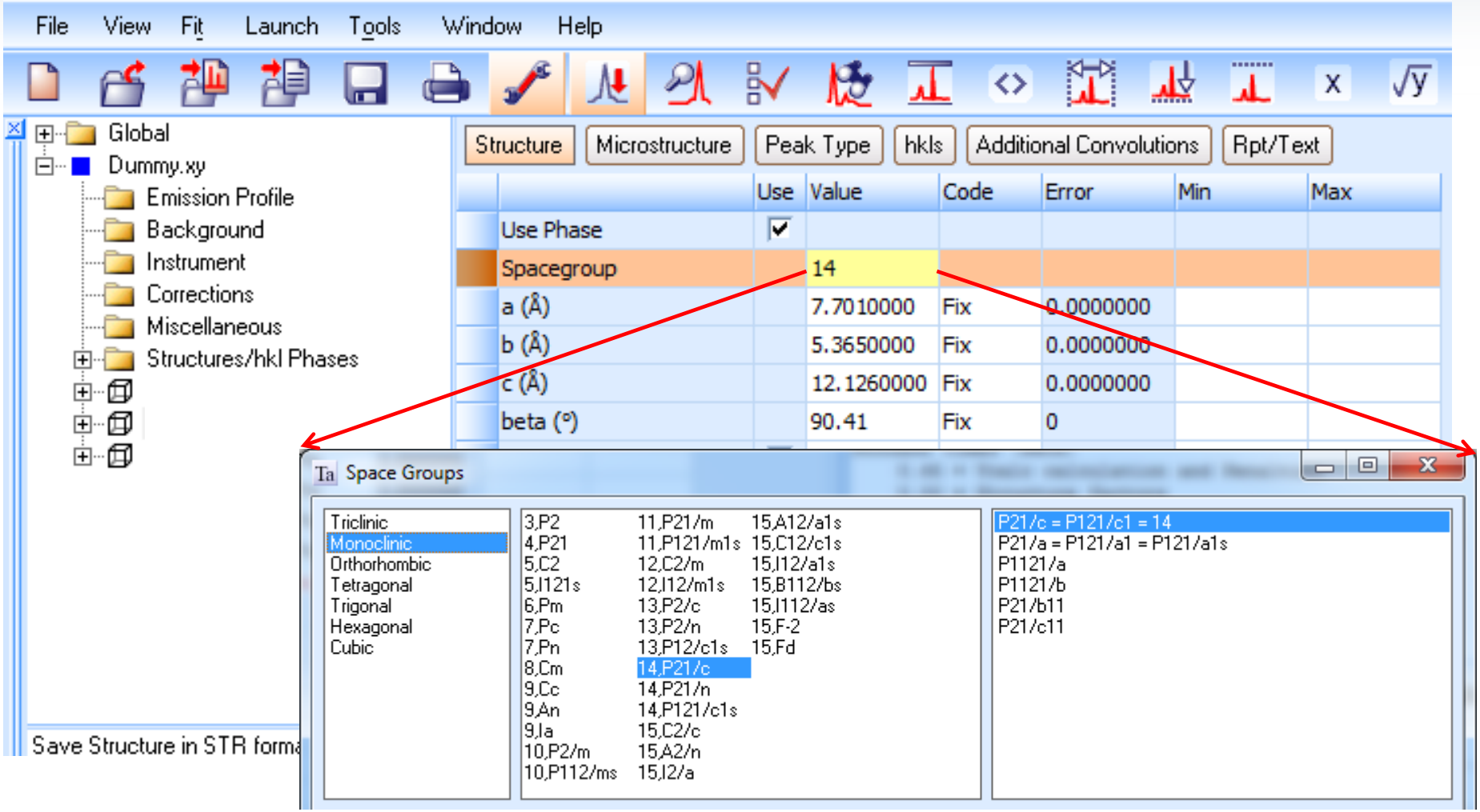
ICDD Pattern ###

2θ	I/Io
13.65	100
14.58	2
18.05	12
23.08	75

Structure as read from database:
For S.G. = 14 software defaults to P21/c

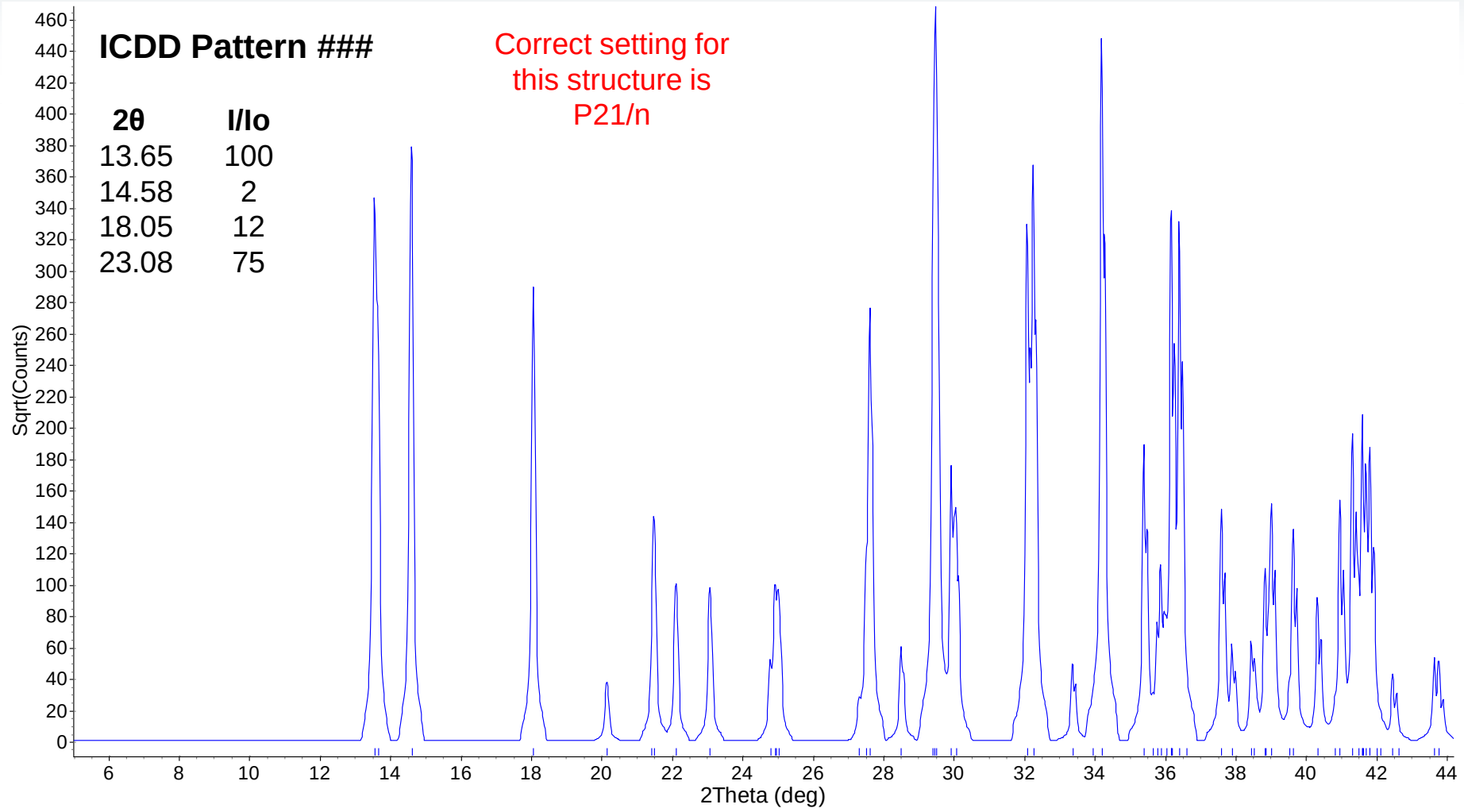


XYZ.3H_2O

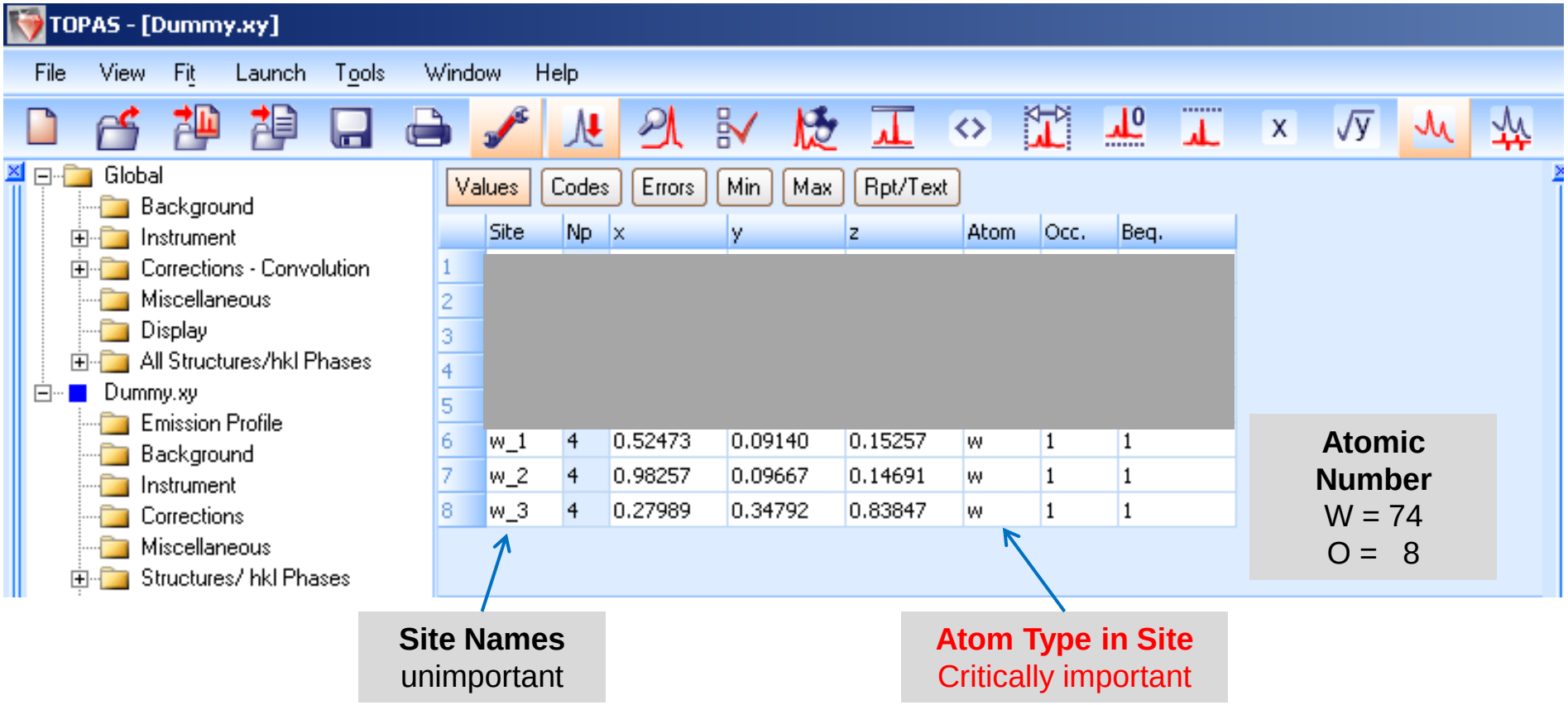

File View Fit Launch Tools Window Help
Global
Dummy.xy
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/hkl Phases
Save Structure in STR forma
Structure
Microstructure
Peak Type
hkls
Additional Convolutions
Rpt/Text
Use
Value
Code
Error
Min
Max
Use Phase
Spacegroup
14
a (Å)
7.7010000
Fix
0.0000000
b (Å)
5.3650000
Fix
0.0000000
c (Å)
12.1260000
Fix
0.0000000
beta (°)
90.41
Fix
0
Space Groups
Triclinic
Monoclinic
Orthorhombic
Tetragonal
Trigonal
Hexagonal
Cubic
3,P2
4,P21
5,C2
5,I121s
6,Pm
7,Pc
7,Pn
8,Cm
9,Cc
9,An
9,Ia
10,P2/m
10,P112/ms
11,P21/m
11,P121/m1s
12,C2/m
12,I12/m1s
13,P2/c
13,P2/n
13,P12/c1s
14,P21/c
14,P21/n
14,P121/c1s
15,C2/c
15,A2/n
15,I2/a
15,A12/a1s
15,C12/c1s
15,I12/a1s
15,B112/bs
15,I112/as
15,F-2
15,Fd
P21/c = P121/c1 = 14
P21/a = P121/a1 = P121/a1s
P1121/a
P1121/b
P21/b11
P21/c11

XYZ.3H_2O – Calculated Pattern

⇨ Space group set to P21/n

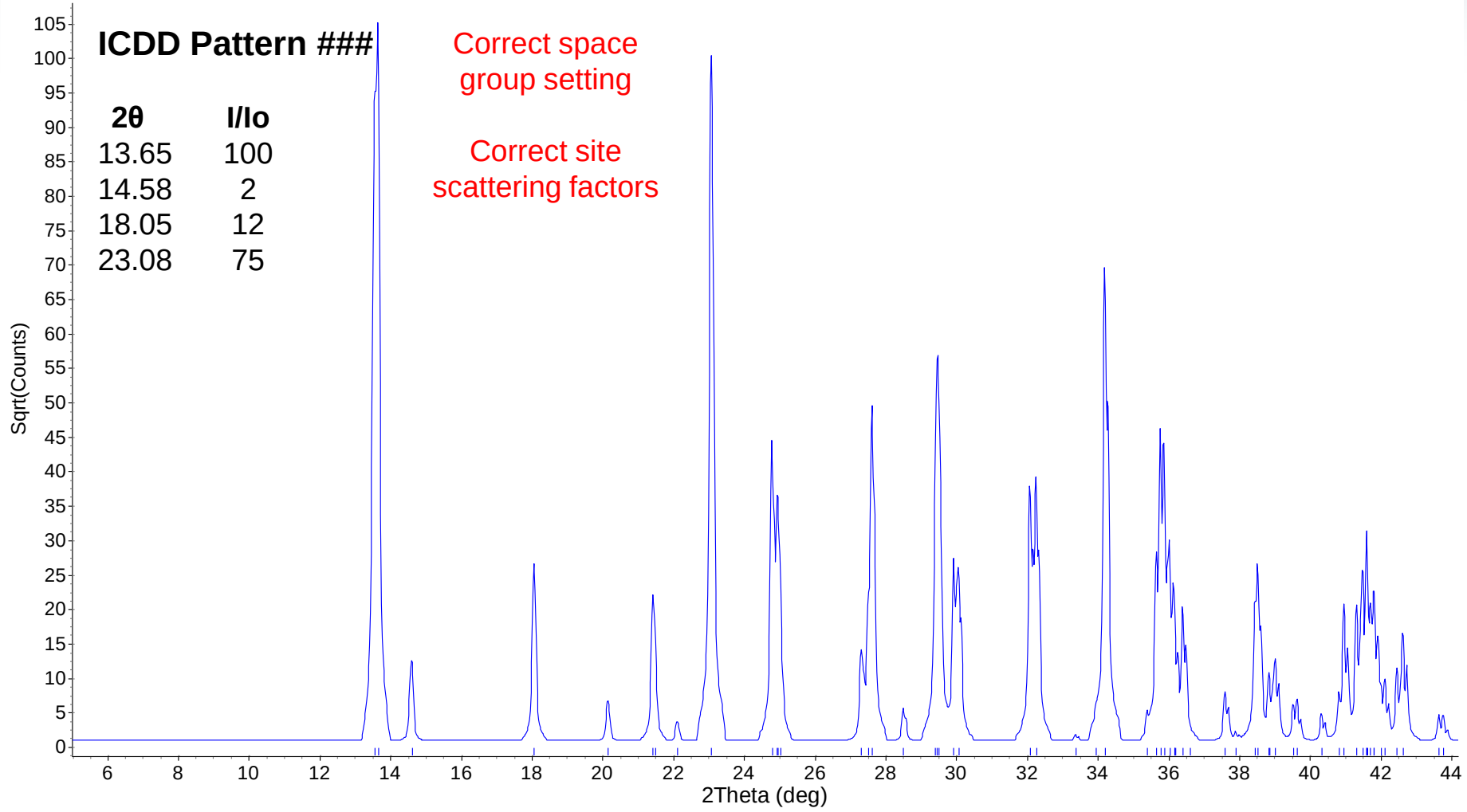


XYZ.3H_2O – Calculated Pattern
⇨ Atomic Sites?



Expected density = 1.84 g/cm^3 Calculated density = 8.51 g/cm^3

XYZ.3H_2O – Calculated Pattern



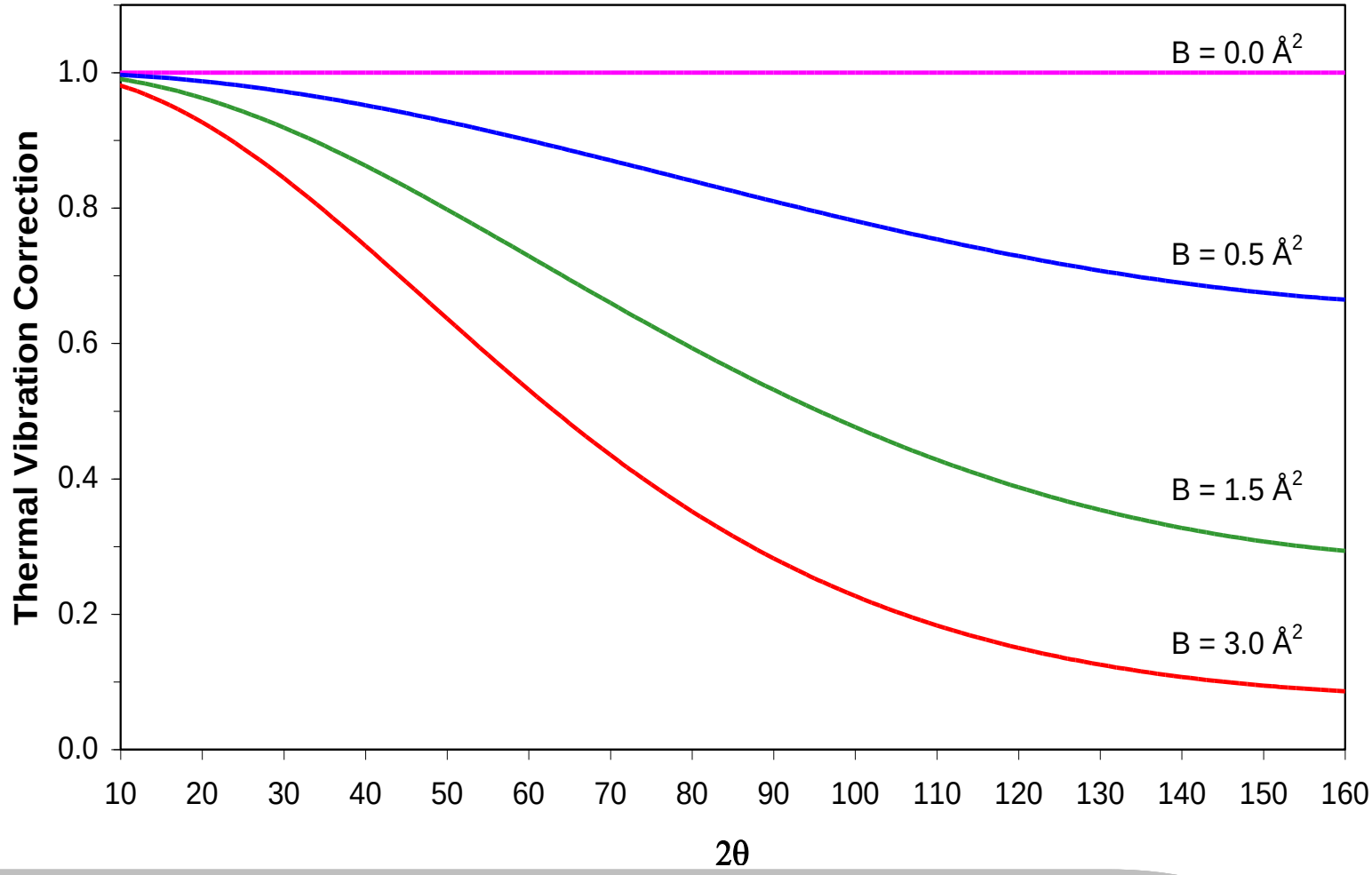
$XYZ.3H_2O$
Database Entry

```
str
   space_group 14     ' Space group (HMS): P 1 21/n 1

   a    7.7053
   b    5.3673
   c   12.1212
   be 90.451

   site                                                                  beq 1.0
   site                                                                  beq 1.0
   site                                                                  beq 1.0
   site                                                                  beq 1.0
   site                                                                  beq 1.0
   site w1     x 0.52473    y 0.09140    z  0.15257    occ O    1.0      beq 1.0
   site w2     x 0.98257    y 0.09667    z  0.14691    occ O    1.0      beq 1.0
   site w3     x 0.27989    y 0.34792    z  0.83847    occ O    1.0      beq 1.0
```

Effect of Atomic Displacement Parameters
⇨ Yet more traps for the unwary

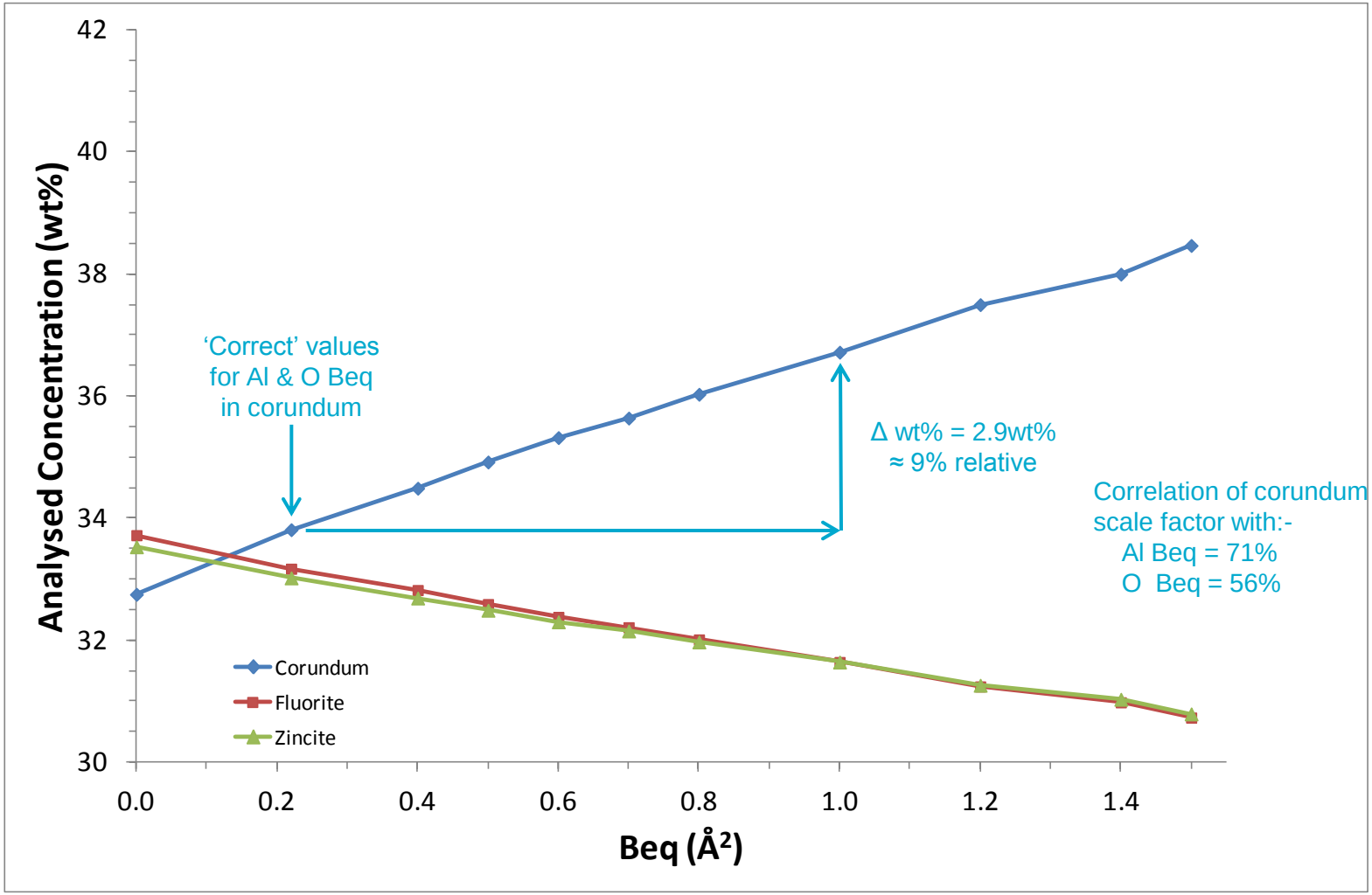
- ADPs correlate strongly with the Rietveld scale factor
  - Hence, ADPs used during analysis will impact on the final QPA
- Many, many crystal structure database entries have arbitrary ADP values entered
  - 0.0, 0.5, 1.0 $Å^2$ for all atoms – view with great suspicion

Intensity Variation with ADP Parameter



Effect of Incorrect ADPs on Phase Abundances

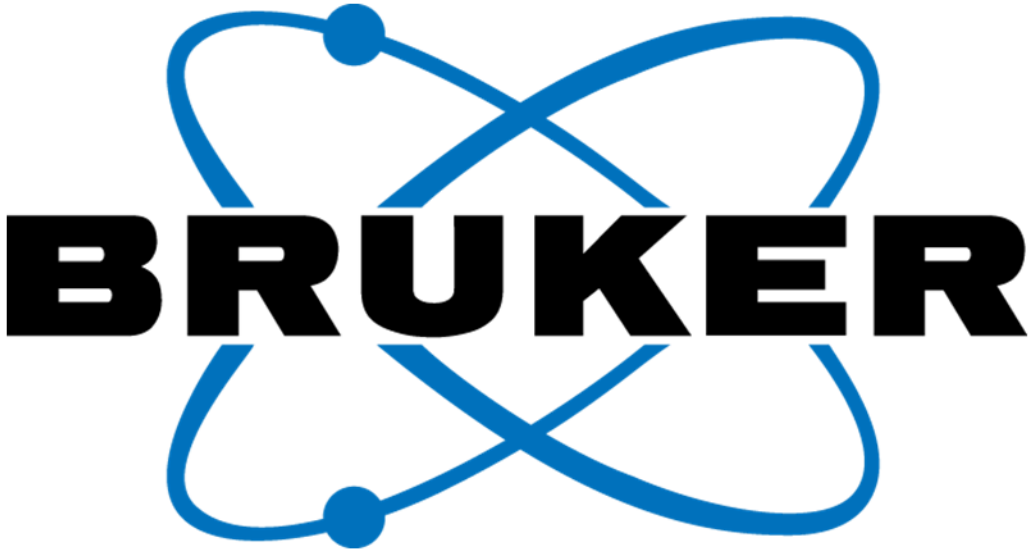
Sample 1G* – QPA *vs* Corundum ADP – ZMV method



* IUCr Round Robin on QPA – Sample 1G ≈ mixture of corundum (Al_2O_3), fluorite (CaF_2) & zincite (ZnO)

Summary

- Verify, verify, verify
- Generate calculated patterns of individual phases
- Check against
  - Data from pure sample of phase
  - ICDD database



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