Energy, Mining and Environment

Laboratory instrumentation
the last 10 years

A reality check?

Pamela Whitfield

Accuracy in Powder Diffraction IV, NIST, April 2013

Overview

- Where we've come from
- The goniometer – heart of the system
- Kinematic-type mounts
- PSDs
- Multi-layer optics
- Selected example application

Diffraction in the lab

- Lab diffractometers often in multi-user environments
- No single setup has been able to satisfy everyone
  - However CuKα Bragg-Brentano with graphite monochromator came closest and was the de-facto standard for years…

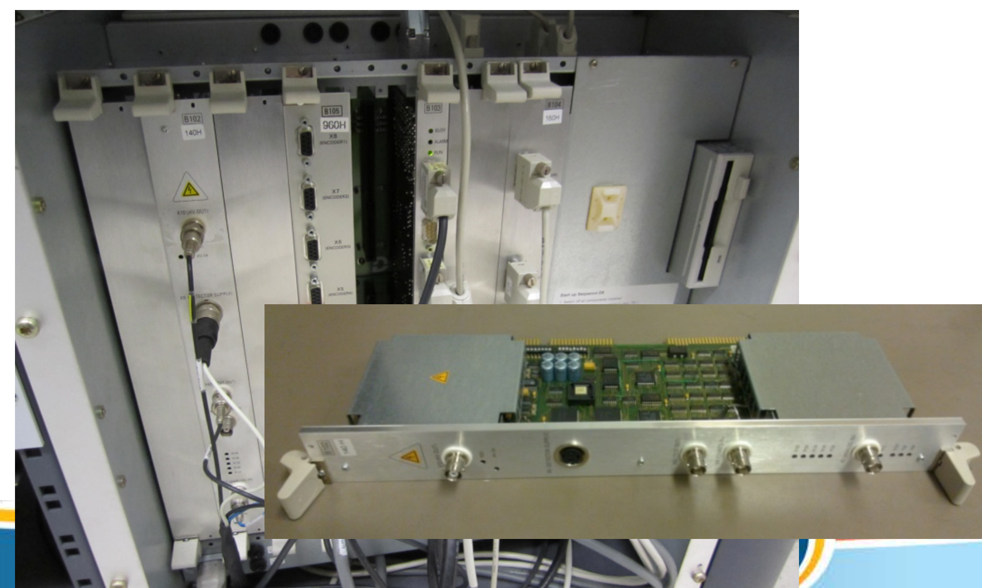
- Simple
- Built like tanks
- Minimal electronics
  - The Scintag XDS2000 has 1 safety circuit that can be defeated with a magnet!

The march of analogue to digital….

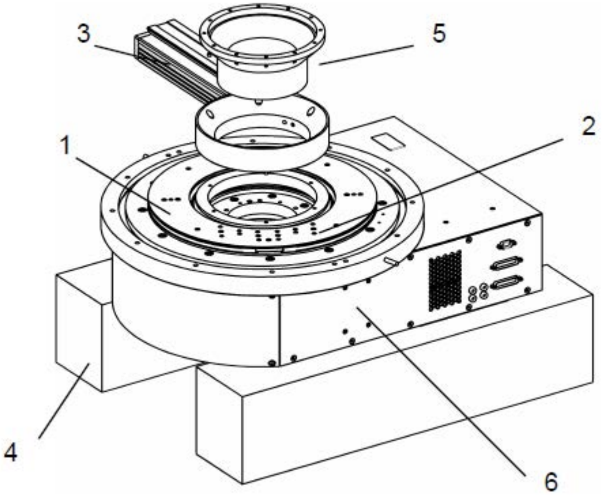
- Systems have become much more complex
  - Systems designed to be flexible and modular
    - The electronics themselves sometimes less so…..
  - More sophisticated microprocessor electronics and safety systems
  - Architectures familiar to anyone who`s looked inside a PC

Old

New



The Goniometer
heart of the diffractometer

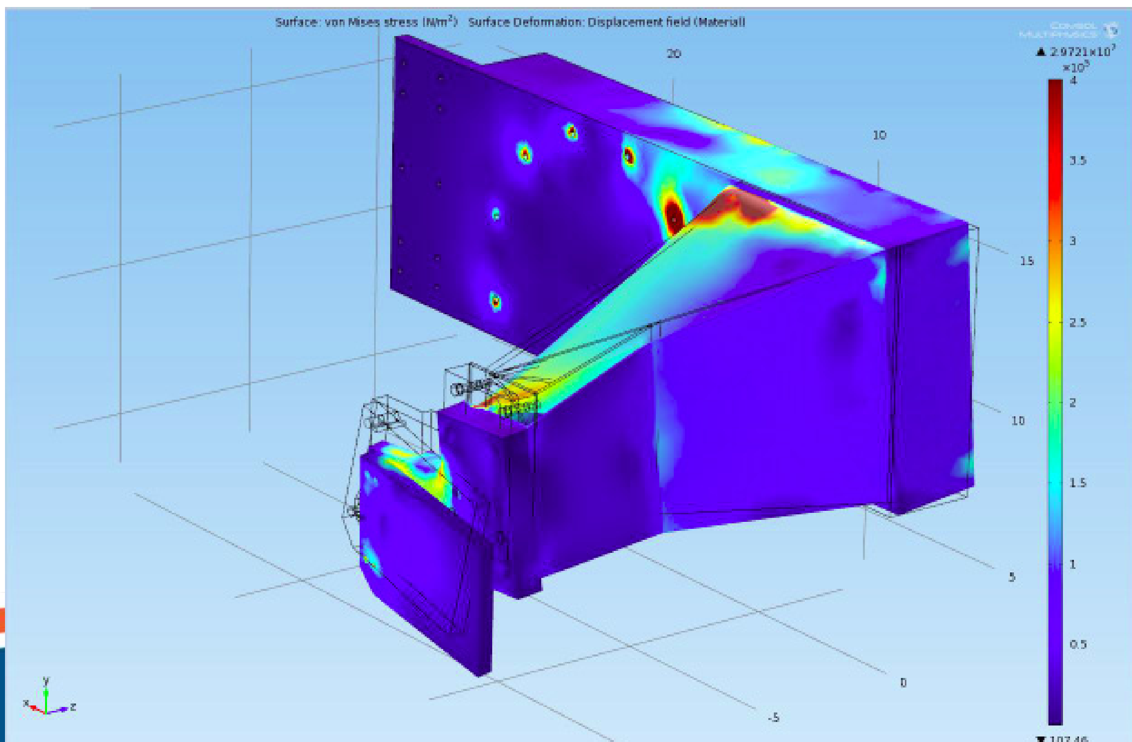


- Basic concept unchanged
  - Axes attached to very large bearings…
    usually ball races
- Drive gears do eventually wear
- Goniometers still largely mechanical but…
  - Optical encoders now widespread to improve positioning accuracy
  - Goniometer arms $\rightarrow$ \`optical benches\`
  - Realignments reduced or even eliminated

Heidenhain RON905 optical encoder accuracy ±0.4”

The Goniometer

- When pushing the limits of accuracy every little matters…
- Flexing of goniometer arm limits accuracy in vertical setup
  - $\rightarrow$ detector/source weight & counterbalancing become issues
- θ–2θ often preferable in terms of pure positional accuracy



Jim Cline being fussy!

Stress analysis on Jim's custom D5000 detector arm

System alignment

- Manual system alignment can be…
  - boring
  - frustrating
  - source of much rude language!
  - impediment to switching configurations
    - – increases my ‘activation energy’

- Don’t have someone with the ‘Midas touch’?
- 2 main alternative approaches
  - Fully motorized and automated alignment
  - Kinematic-type mounts for reproducibility

Automated alignment

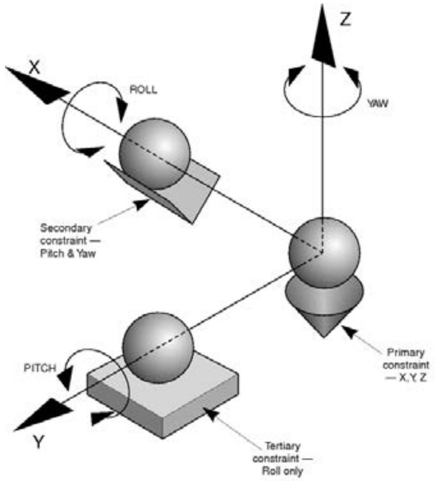
- Alignment automated at the touch of a button
  - Everything motorized and software controlled
  - Easy for the user

- However, system never exactly the same twice after realigning
  - No different from manual realignment in this regard

- System reproducibility shouldn't change over time
  - Mechanical wear excepted

Kinematic mounts

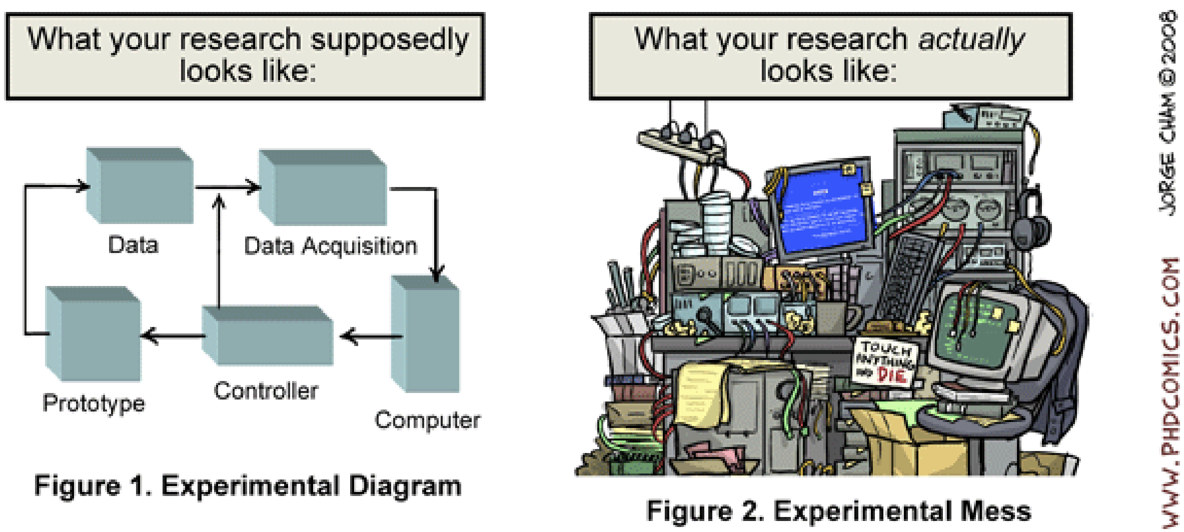
- Kinetic mounts used routinely for mounting optical mirrors
  - 3-leg stool (tripod) concept



3-point kinematic mirror mount

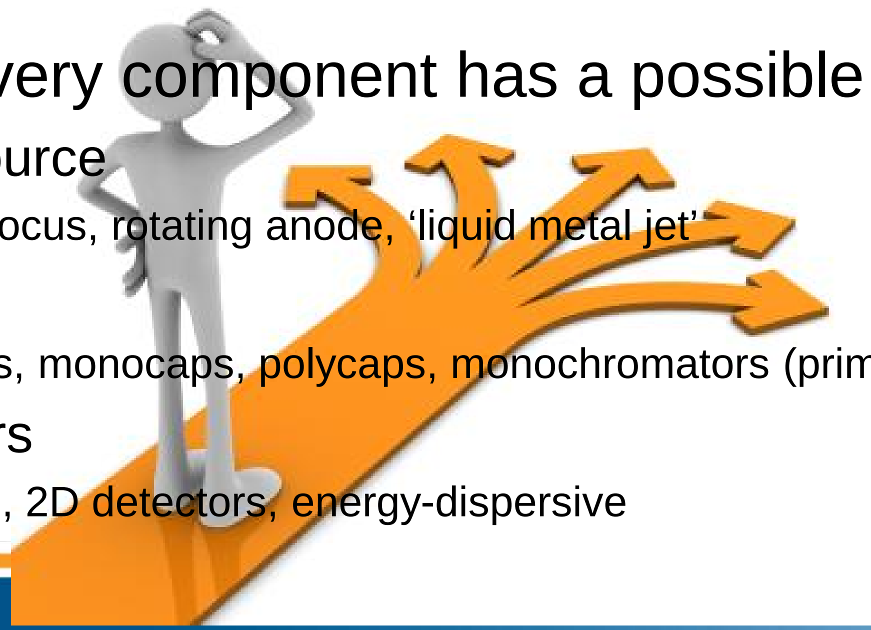
- Dirty environments?
  - Forces *should* force dirt out from between surfaces – no effect
  - However, turbidity from environment/surfaces *can* prevent equilibrium being reached
    - Chocking effect (www.precisionball.com/kinematic_encyclopedia.php)

- Precision engineering – expensive!
- Hardened surfaces desirable (e.g. WC)
  - Reduce contact distortion + low friction
  - High shear strength to resist lateral forces (chocking)
- Mounts need to be robust
  - Delicate stuff tends to not fare well in a university environment!
- Factory-aligned
  - Portability between multiple systems?



From the old to the new…..

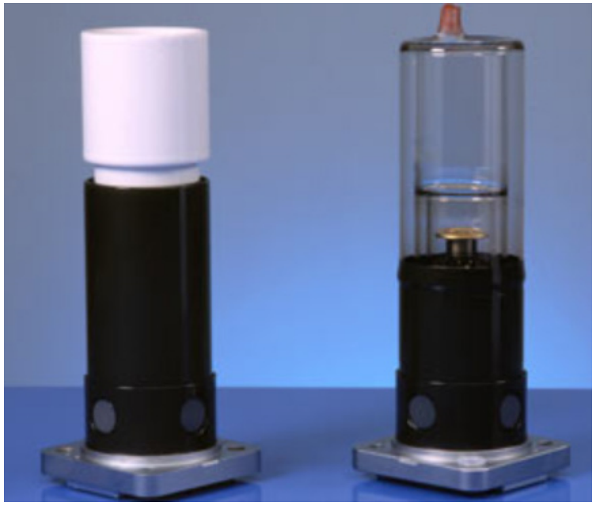
- Bragg-Brentano + graphite mono/scintillation detector
  - gives excellent data but low counts
- Fear not!
  - Many new toys to spend your money on!



- Seems every component has a possible upgrade
  - X-ray source
    - Microfocus, rotating anode, ‘liquid metal jet’
  - Optics
    - Mirrors, monocaps, polycaps, monochromators (primary and secondary)
  - Detectors
    - PSDs, 2D detectors, energy-dispersive

X-ray sources

- Standard X-ray tube still the most common source
  - Ceramic insulation used increasingly
  - Ceramic is a better heat-conductor
  - Better tube lifetime claimed



GE X-ray tubes

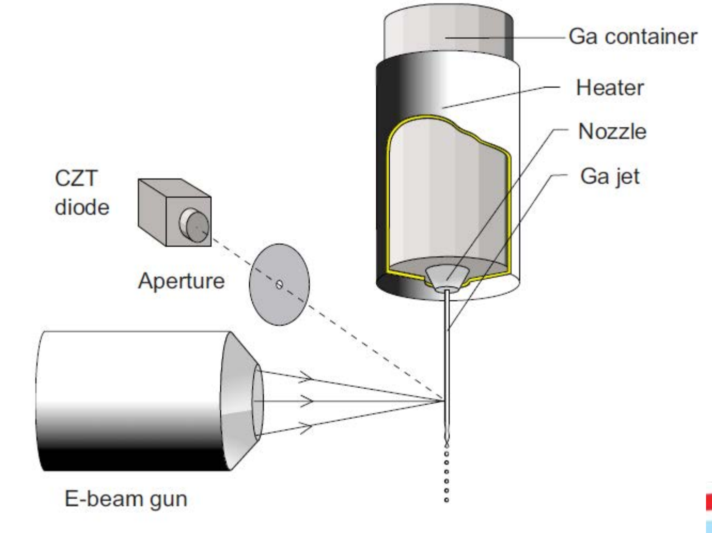
- Rotating anode
  - Still quite a niche product for powder diffraction
  - Large increase in tube power (↑ 18kW)
  - Generally very heavy and bulky
    - Not normally used for θ–θ systems due to issues mentioned previously but….

Rigaku TTRAX

Spot-focus X-ray sources

- Microfocus
  - Widely available
  - Standard anode materials
  - High brilliance
    - Comparable to older synchrotron beamlines

- Liquid-metal jet
  - Don`t have to worry about melting the anode as it`s already liquid
  - Wavelength GaKα (other metals as dopants in liquid)
    - GaKα similar to CuKα but users often uncomfortable changing wavelengths..

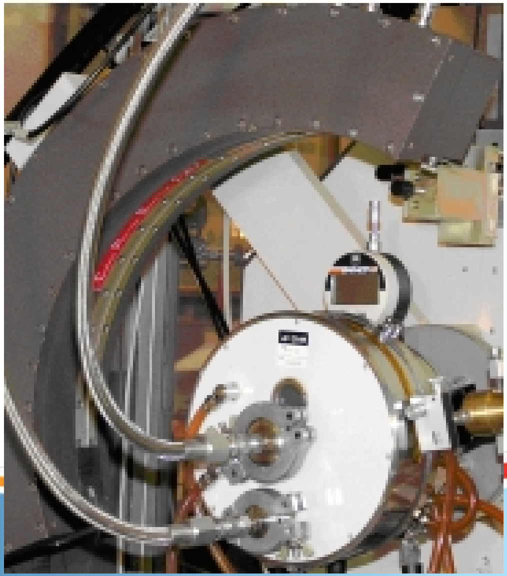


Position Sensitive Detectors rule?

- Historically proportional detectors using a counting gas
  e.g. mBraun, Inel
- Calibration required to relate ‘channel number’ to angle
- Defocussing in linear PSDs
- Inel known for their curved PSDs
  - No defocussing but calibration functions more complex

mBraun PSD

Inel 120° PSD



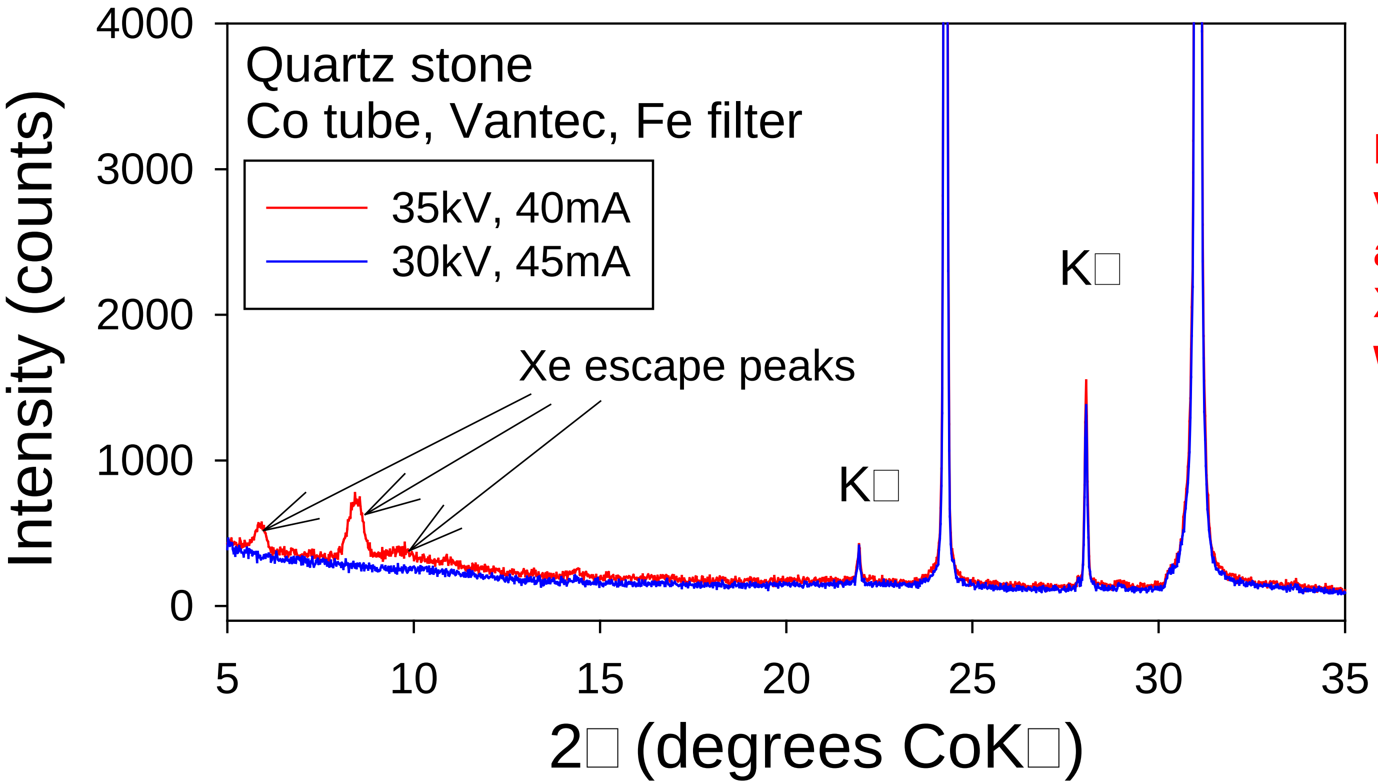
PSDs rule!

- PSDs largely moved away from gas-based technologies
- PSDs now a common sight in XRD labs
  - What effect has this had on aspects of accuracy?
- GOOD
  - Count rates…
  - Excellent signal-to-noise

- BAD
  - Count rates!
  - Artefacts in data now visible

Newer PSD technologies

- More advanced gas-based counting (e.g. Vantec-1)
  - 33keV Xe escape peaks can be problematic
    - not all detectors the same…. one of ours less sensitive then the other
  - Works up to MoKα (Vantec AgKα ✗)

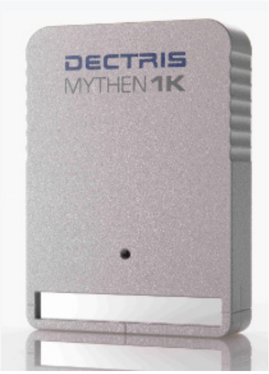


Effect of generator voltage on appearance of 33keV Xe escape peaks without primary optic

Solid state strip detectors

- Current mainstream PSD technology

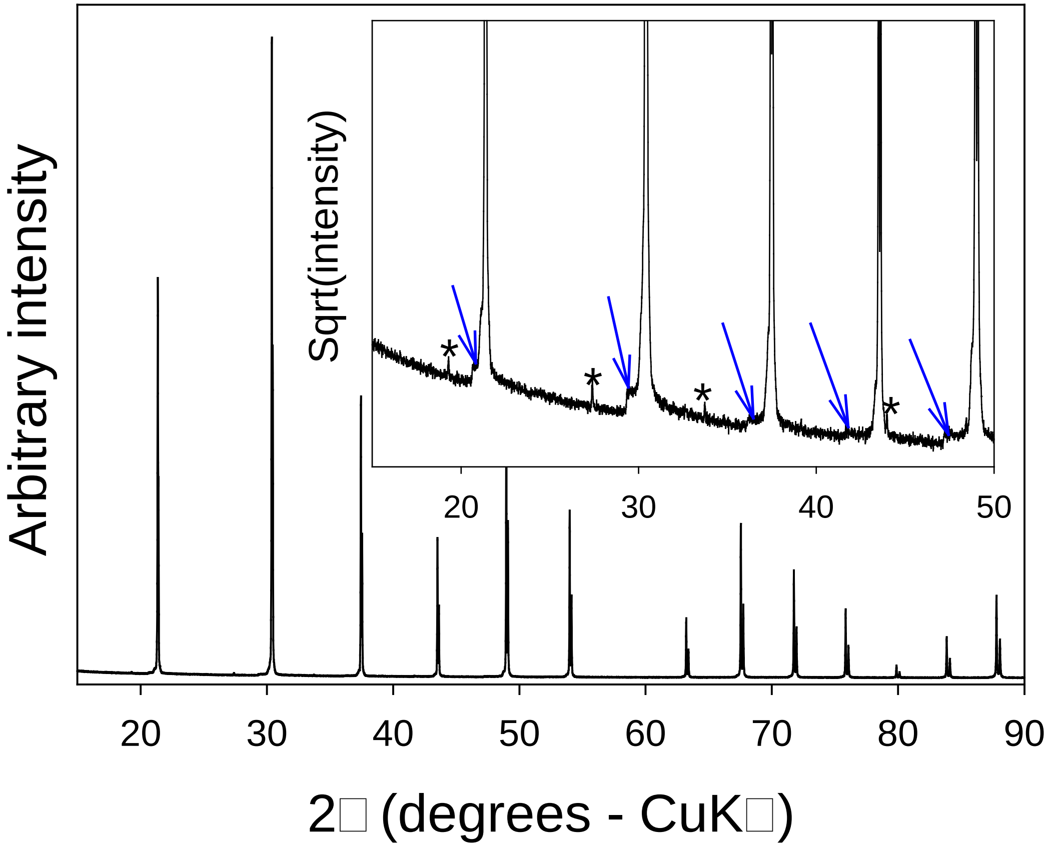




- Cost effective
- PSD energy discrimination improving
- Higher X-ray energies require thicker Si films to maintain efficiency
- Image-plate based curved PSD - Stoe

PSDs rule! – not so good?

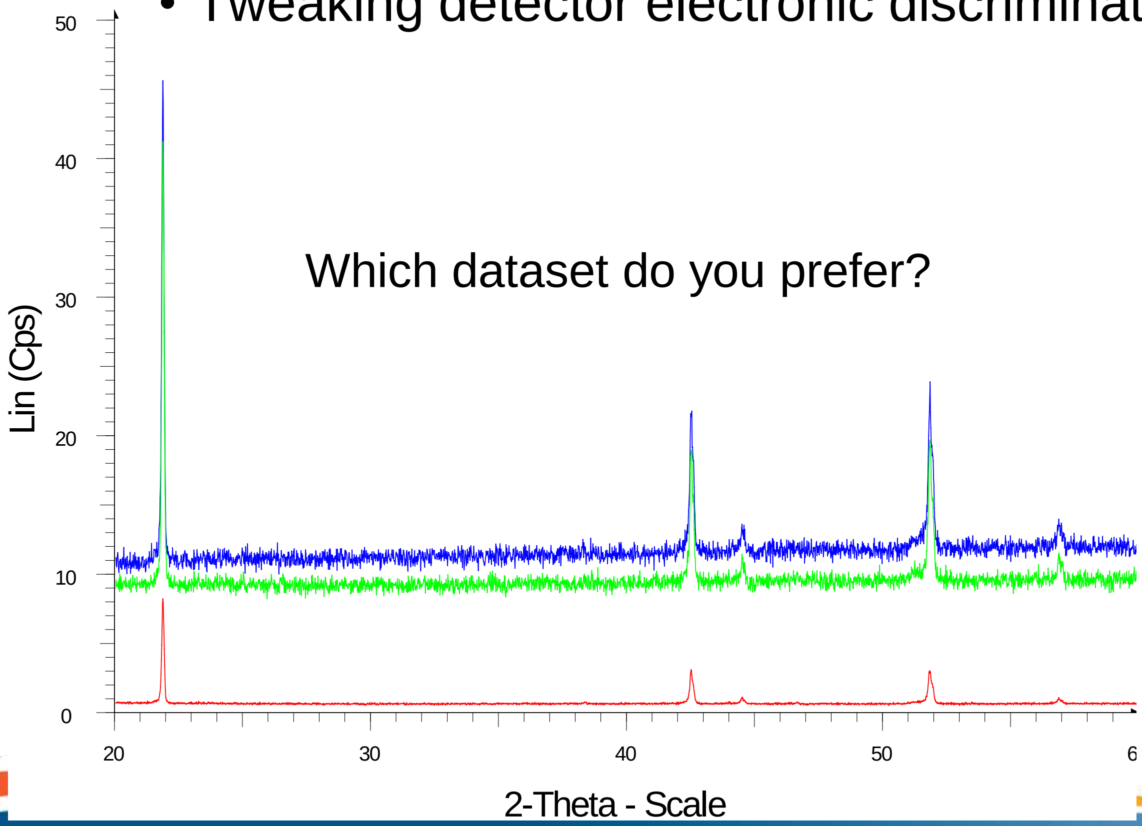
- More stuff you`d rather ignore
  - Absorption-edges of Kβ-filters
    - Background fitting errors → inaccurate peak intensities
  - Tungsten Lα lines & residual Kβ intensity becomes very obvious



LaB$_6$ with CuKα and a nickel Kβ filter

PSDs

- Normally poor energy discrimination
  - In absence of monochromator fluorescence a major problem
  - Poor peak-to-background impacts accuracy (CPD Rietveld RR)
  - Tweaking detector electronic discriminators can help…



$LiMn_{1.5}Ni_{0.5}O_4$

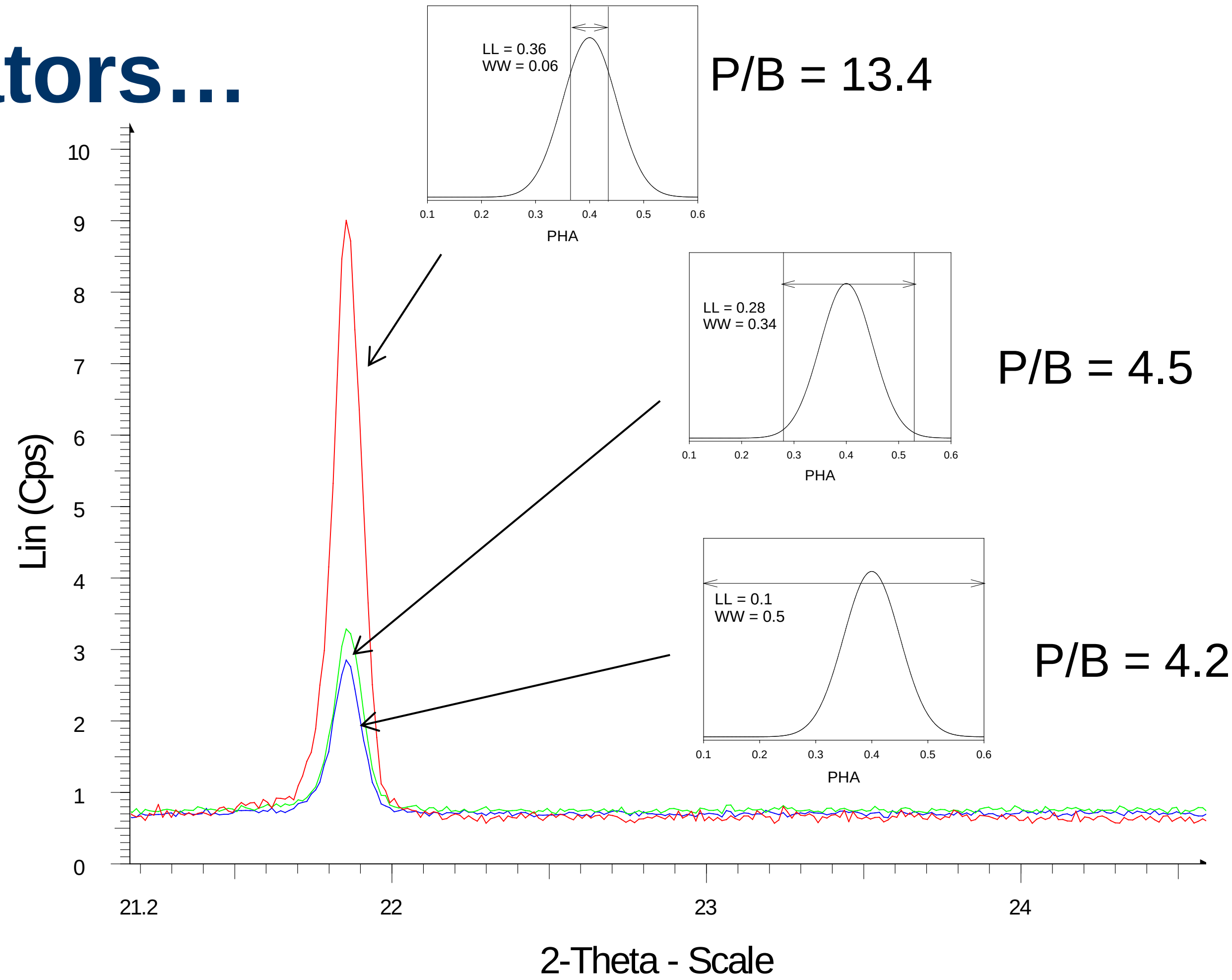
CoKα with varying detector discriminator settings

Discriminators…

Rescaled to normalize background

Sacrifice intensity to improve P/B ratio

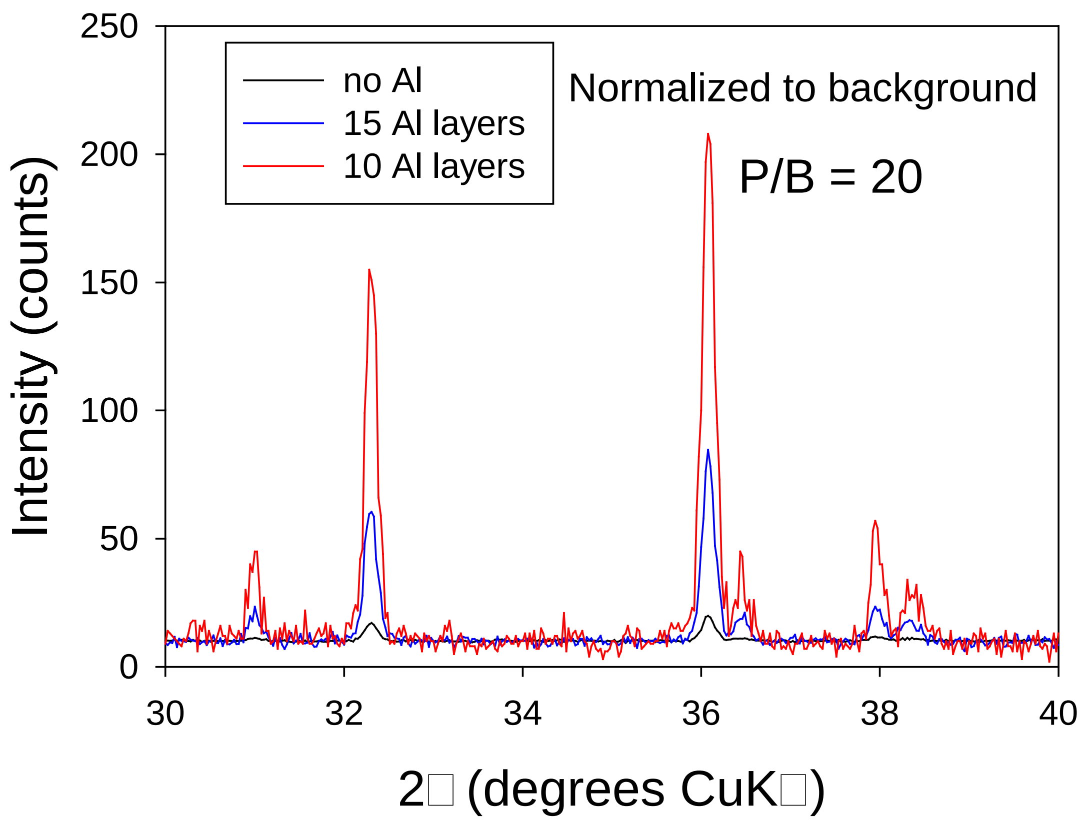
P/B still way off 50



- Recent developments in electronics have greatly improved possible energy discrimination of PSDs

Alternative low tech approach…

- High-purity Al foil filters can reduce fluorescent background
  - costs intensity
  - but once again less can be more!

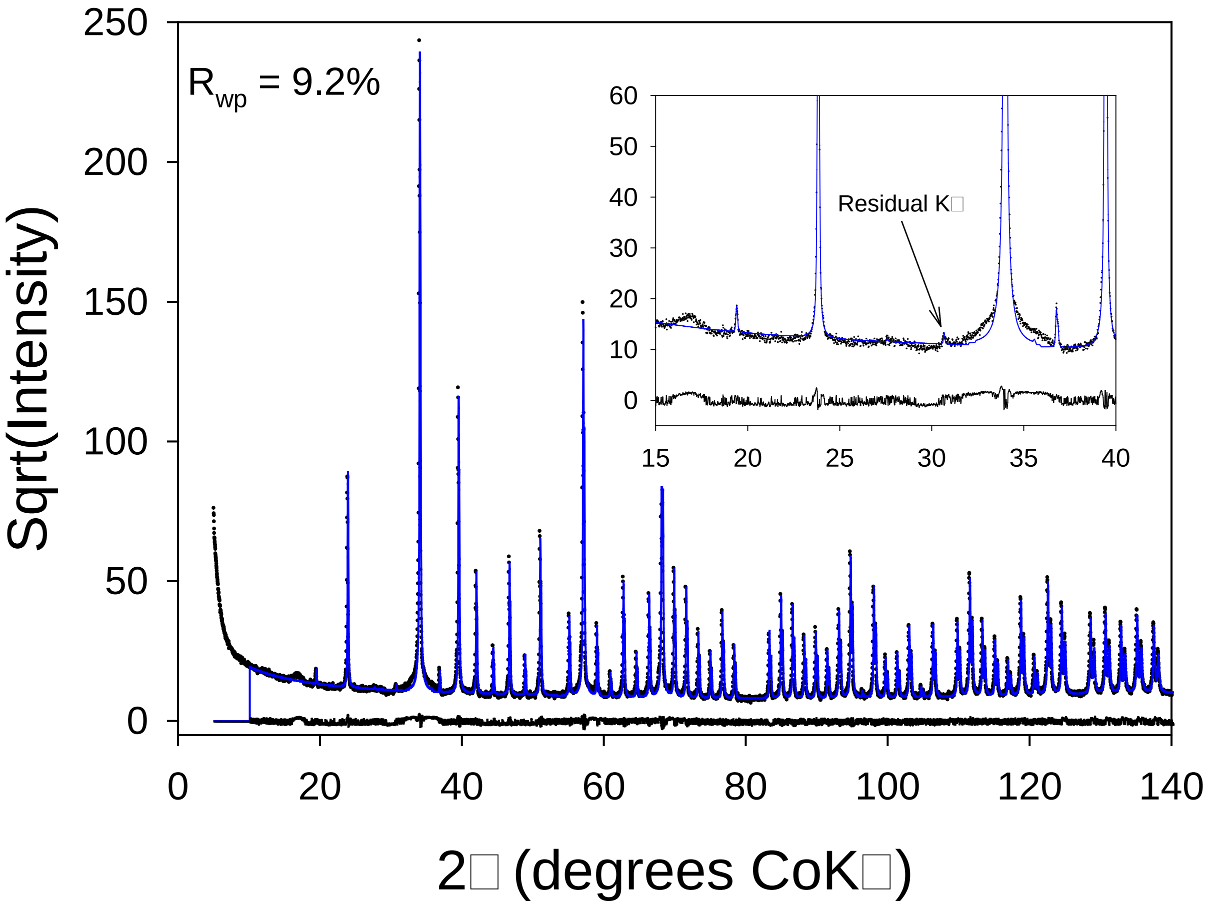


Mn_3O_4
CuKα
primary mirror
mBraun PSD
Al foil mounted on Ni filter

Data from Ian Madsen

PSDs and monochromators…

- Out-of-plane monochromators fitted to some PSDs
- Gets rid of fluorescence but can cause other issues



Y_2O_3 data from an APD system

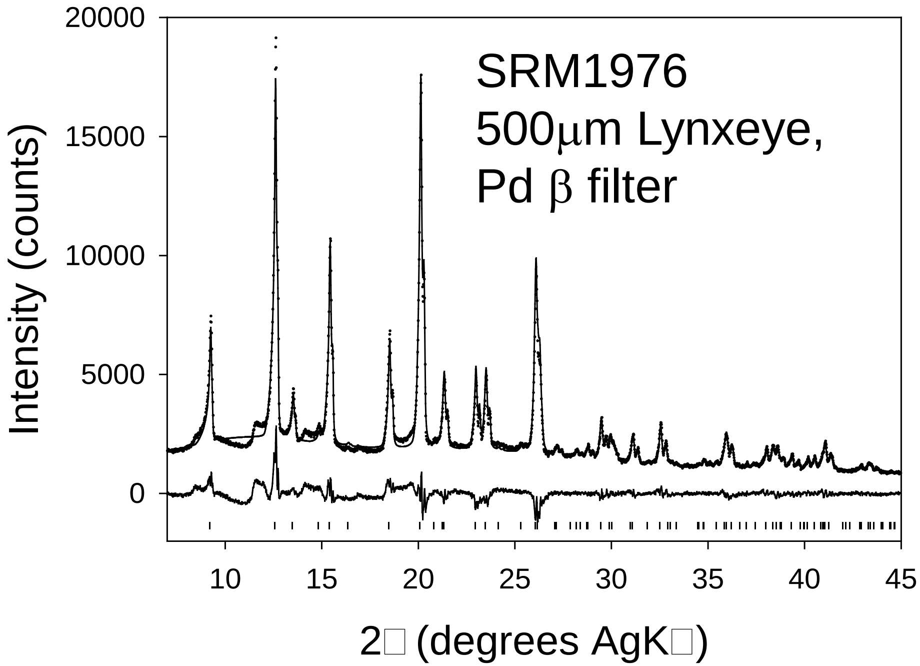
Bragg-Brentano proportional 0D detector graphite monochromator

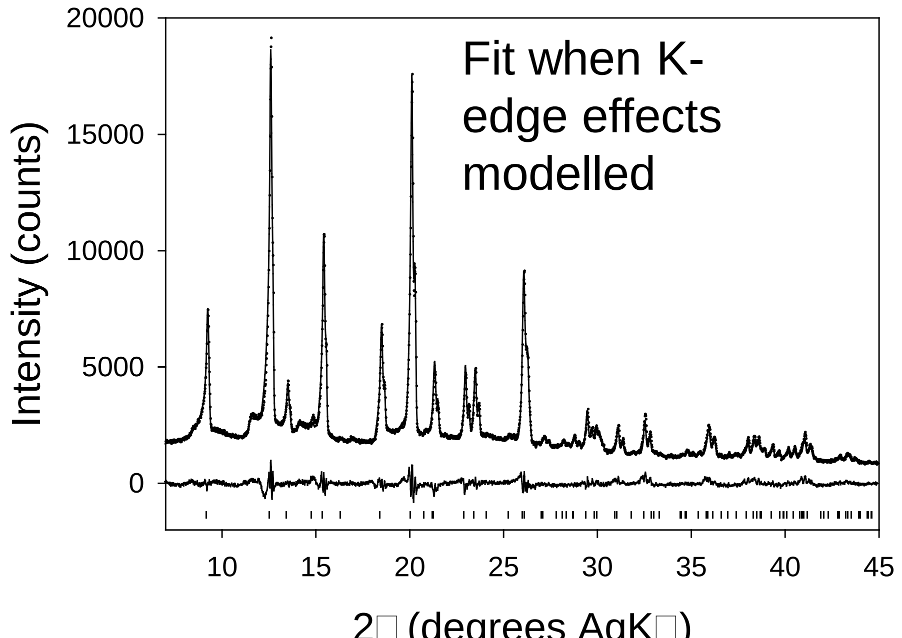
Y_2O_3 data from an MPD system

Bragg-Brentano PSD strip detector with monochromator

PSDs – flexibility?

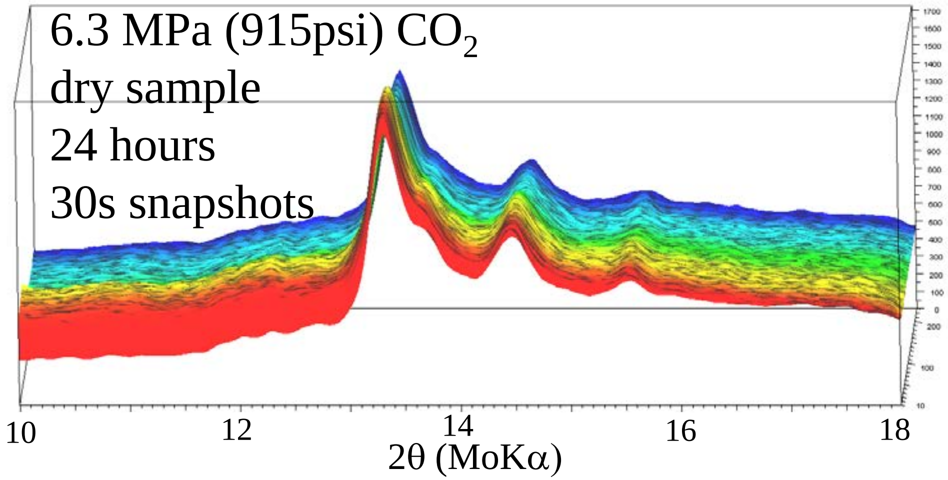
- Most lab-based PSDs optimized for CuKα
  - MoKα – reduced efficiency even if it works….
  - AgKα – good luck!
- Detector electronics may need better shielding
- Absorption edge from β filter difficult to miss with MoKα & AgKα!



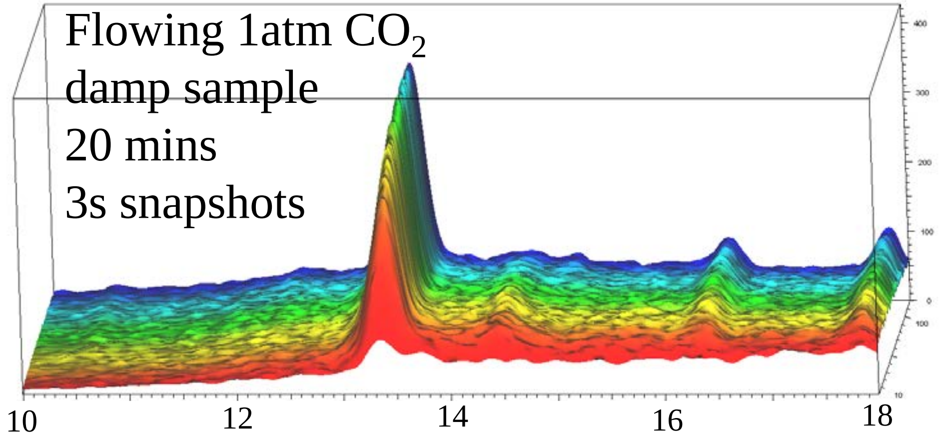


However - all is not lost…..

- E.g. PSD not optimised for MoKα …
- Calcium silicate hydrate (CSH) carbonation
- Fixed snaphots - 8°

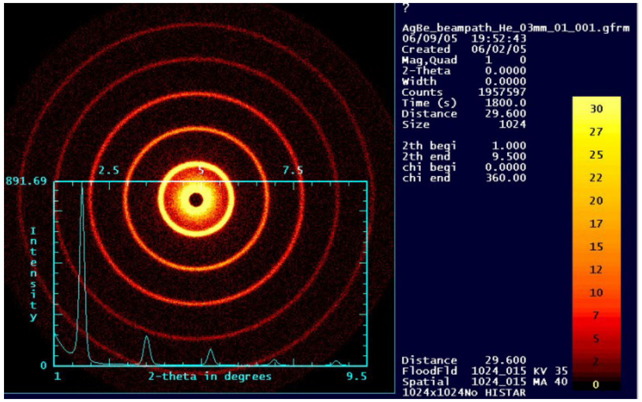


- Damp sample vs dry
- Damp sample 3s time resolution



2D detectors

- Common at synchrotrons
- Increasingly in lab as well…



- Positional accuracy more problematic as more sources of error in calibration
  - Complex aberration functions
  - With lab wavelengths integrated data from multiple frames may have to be merged…
- We never used ours much – too many Mn-rich samples
  - Fluorescence a real problem with either CuKα or CoKα
  - Al foil filter also works with 2D detectors but not ideal…
  - Currently sat in a box!

Multi-layer Mirrors….

- Technologies for multilayers developed over last 10 years
  - The layer materials in use have evolved
  - Mirror corrosion issues solved
- Originally only CuKα widely available
- Now available in all wavelengths in divergent/parallel/ convergent
- The right mirror for the right application can be great

Fraunhofer 40mm CuKα W-based mirror (circa 2002)

Incoatec sealed 60mm CuKα Ni-based mirror (circa 2006)

Multi-layer mirror optics

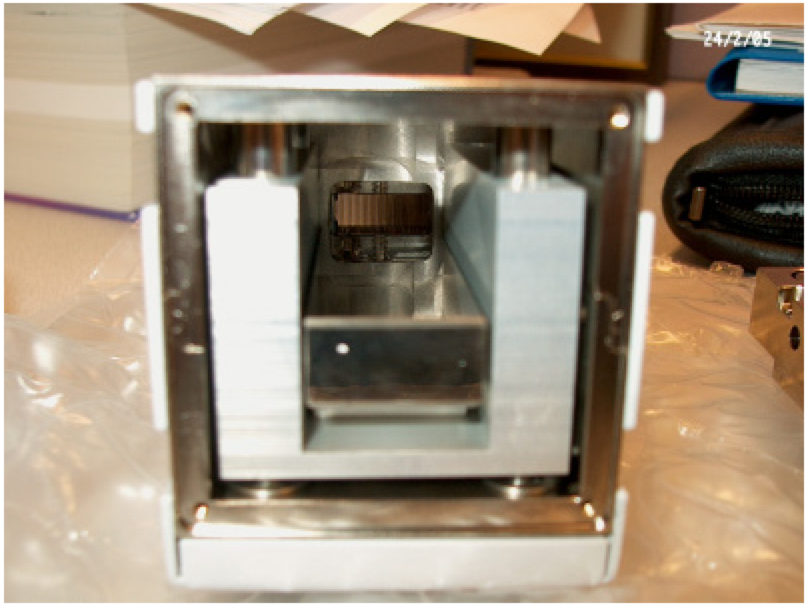
mirrors versus monochromators – pros & cons

- Pros
  - Choose from convergent, parallel or divergent
  - Very high intensities possible
  - Excellent $K\beta$ suppression
  - Good resolution can be achieved in focussing geometry

- Cons
  - Wavelength specific
  - $K\alpha 1/K\alpha 2$ doublet
  - Past history of surface corrosion
  - Temperature sensitive

- Despite cons I have an unsealed $CuK\alpha$ focussing mirror

Not for those of a weak disposition…!
Horror pic from 2005



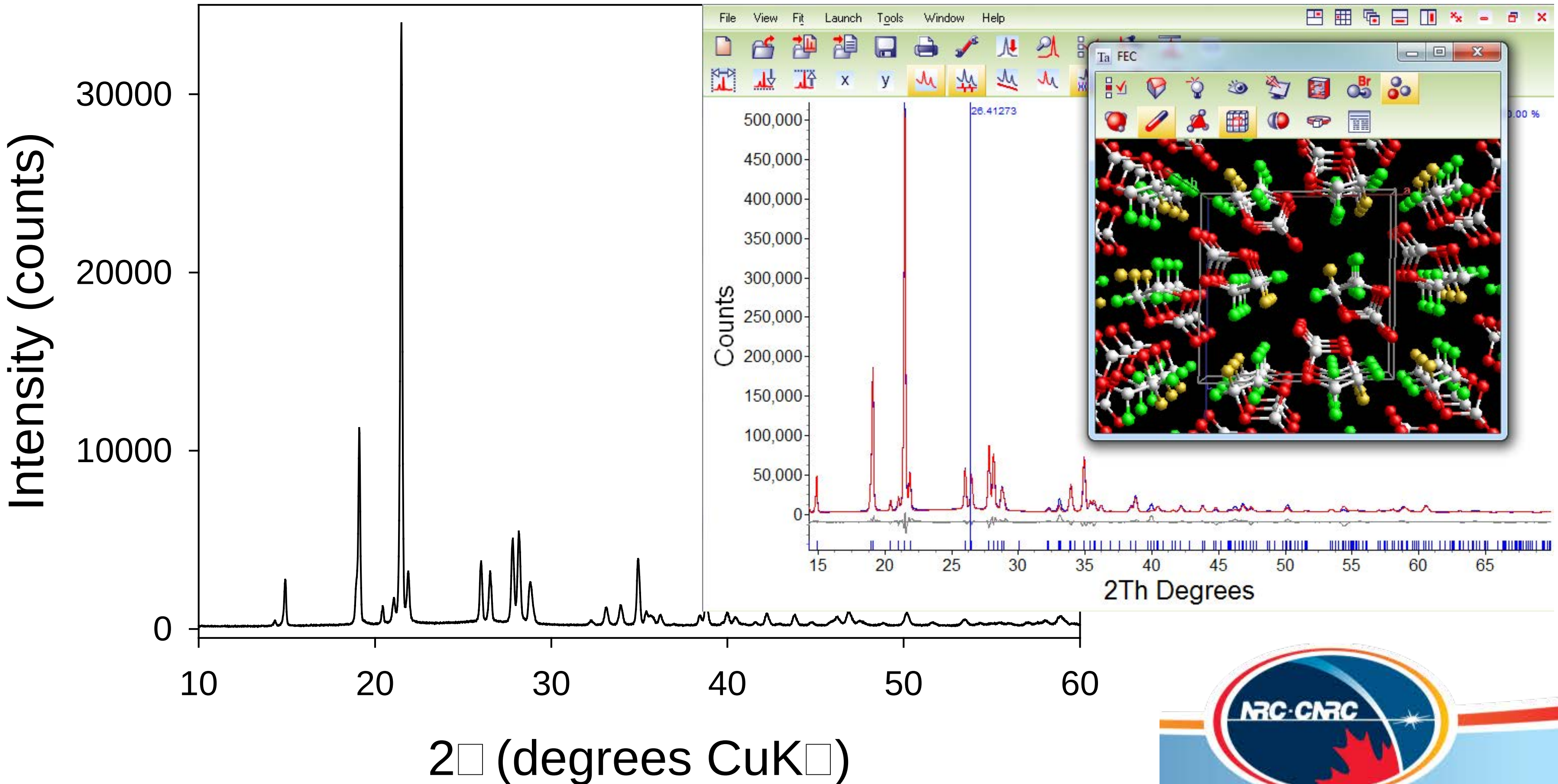
A nice new 'mirror-like' mirror

After intensities started to drop…

- Eventually explained by ozone attack
- Sealed units or inert flowing gas solved problem…
  - or reduce Bremmstralung energy by reducing voltage

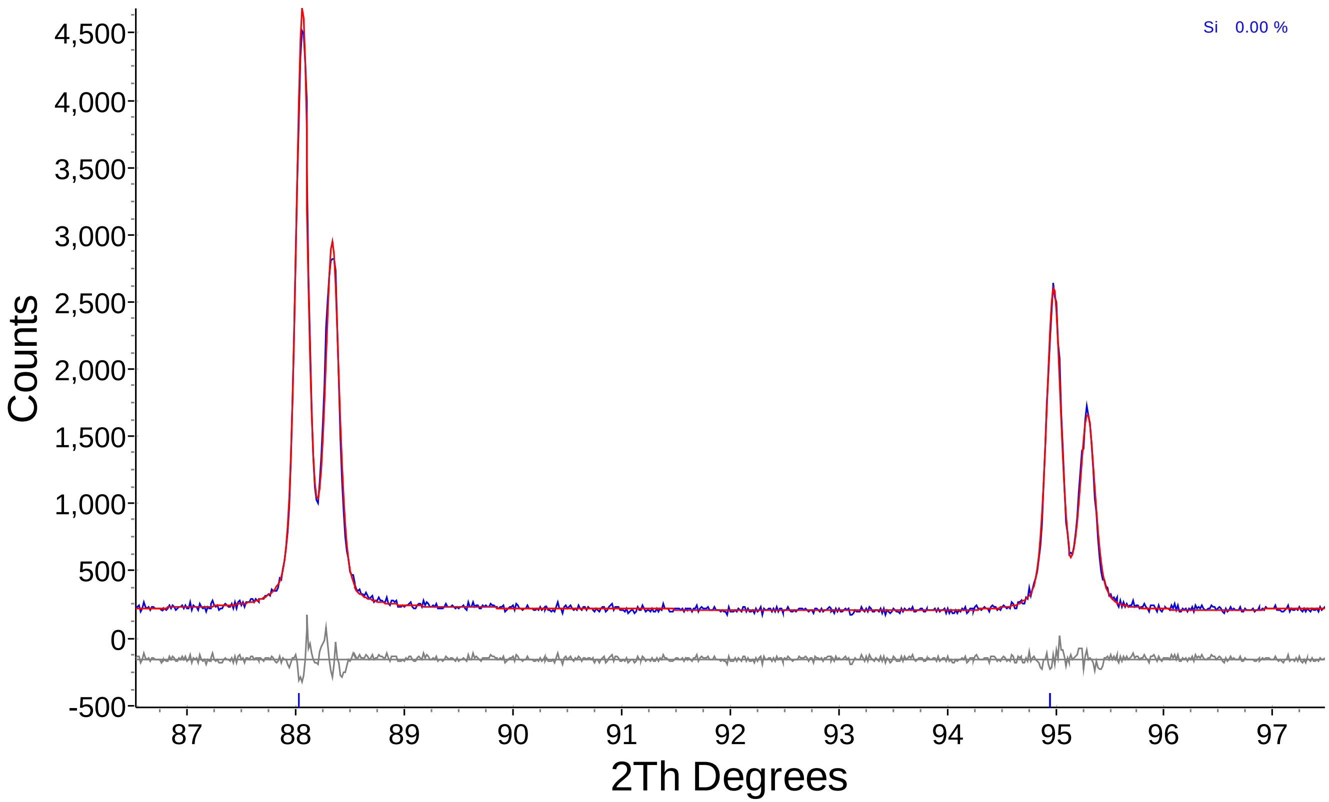
CuKα focussing mirror – Pro (intensity)

- Fluoroethylene carbonate (focussing mirror + 10° PSD)
  - Structure indexed using a 4 minute dataset
  - Solved & refined with 3.5hr pseudo-VCT dataset → 140° 2θ



CuKα focussing mirror – Con (odd profile)

- Can be tricky to get Kα2 at 50% during manual alignment
  - The change easily modelled but not ideal
- Alignment for max intensity often doesn't give best result….



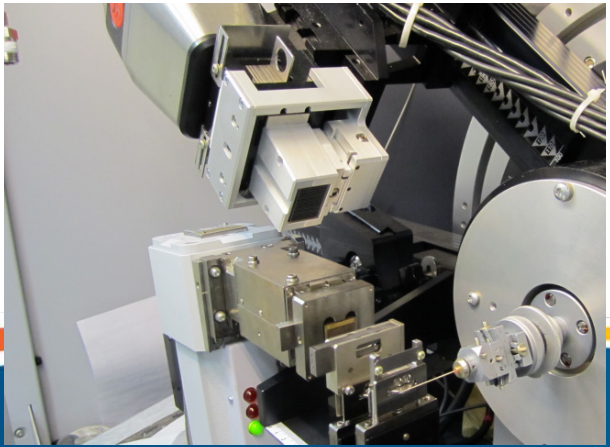
SRM640c
Kα2 = 63%

(simple 2 line emission profile)

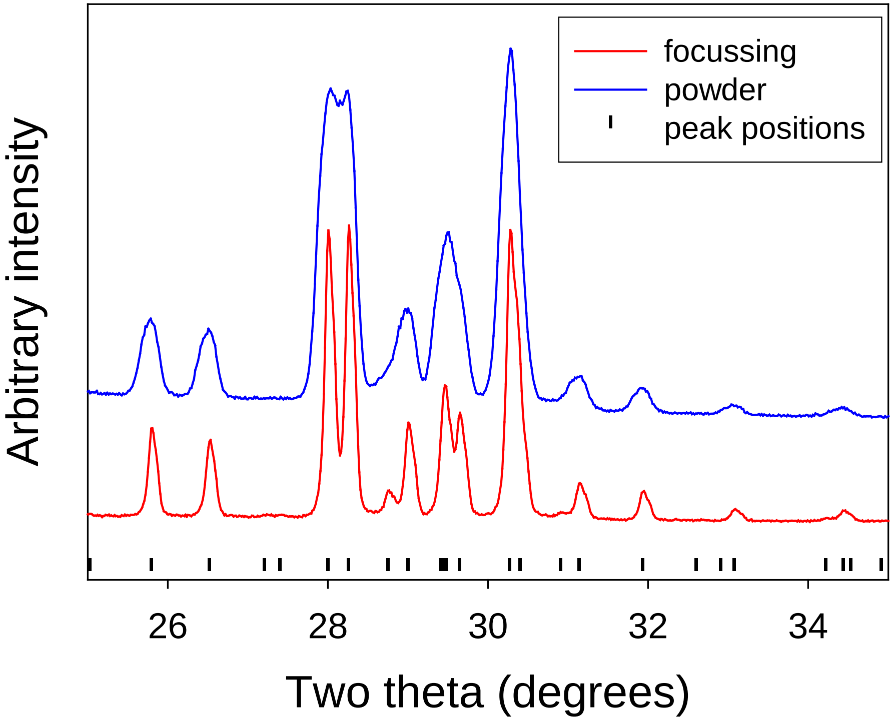
Multi-layer mirrors

- Make sure you have the right one for the job…
- Parallel-beam mirror should have been fine for capillary transmission work
- Divergent ‘powder mirrors’ can be problematic
  - strange peak shapes, poor resolution

Focussing for transmission



Comparison of capillary data from jadarite with a ‘powder mirror’ and a focussing mirror

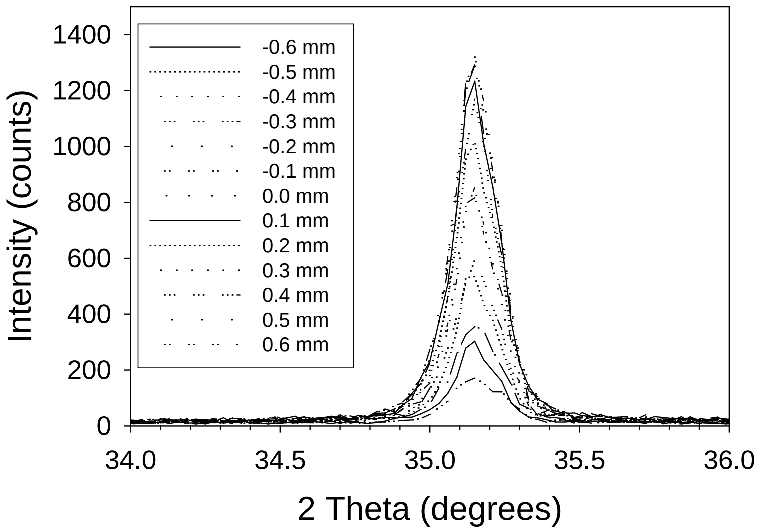


Twin mirrors

- Second mirror focuses onto scintillation detector
  - decent peak resolution
  - excellent backgrounds
  - the data is still student-proof!
- Quite rare….and not cheap….
- Particle statistics aren't great

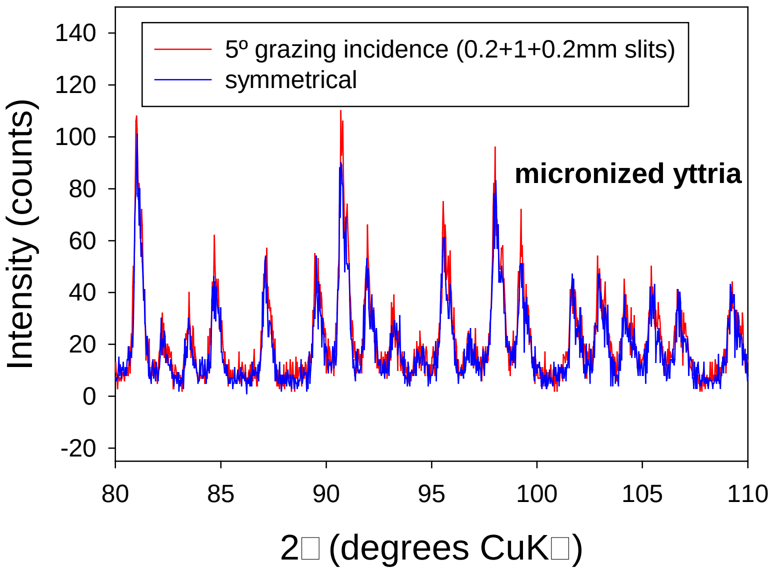
Oddity? 60mm Ni-based sealed primary with 40mm W-based unsealed secondary….

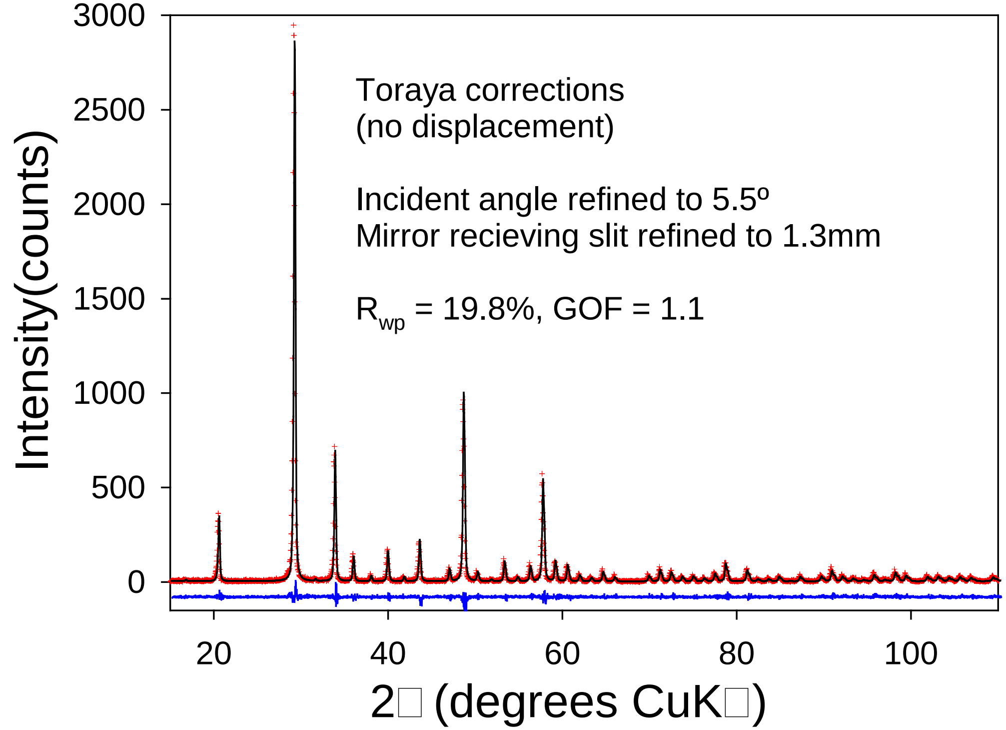
Al_2O_3 104 reflection with displacement for contoured sample



Grazing incidence with twin mirrors…

- Secondary mirror → no loss of peak resolution
- Complex intensity/angle relationship but can be modelled
  - Dependence gets quite ‘interesting’ with sample displacement…

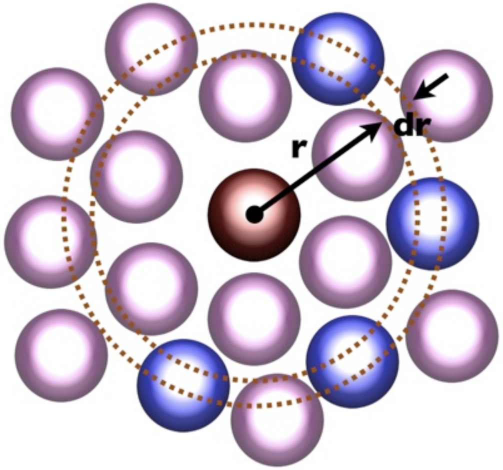




Increasingly Popular Application Areas

- Combinatorial screening
  - 2D detectors with well plates
- Pharmaceuticals
  - Polymorphs and structure solution
- Tomography
- Residual stress
  - 2D detectors
- Pair Distribution Function (PDF)
  - High energy

Pair Distribution Function



- Synchrotron beam-time a finite resource
  - Lab studies viable for some systems where resolution not as vital
- Was always possible but painfully slow with lab instrumentation

Apologies for the pun!

- Need very low noise to high scattering angles
  - PSDs desirable but efficiency ↓ as energy ↑

PDF – instrument considerations

- Want highest-energy to maximize Q-range, but…..
  - MoKα – Q_{max} ~18 Å^{-1}, 3kW LFF tubes
  - AgKα – Q_{max} ~22 Å^{-1}, 1.5kW LFF tubes (50kV, 28mA)

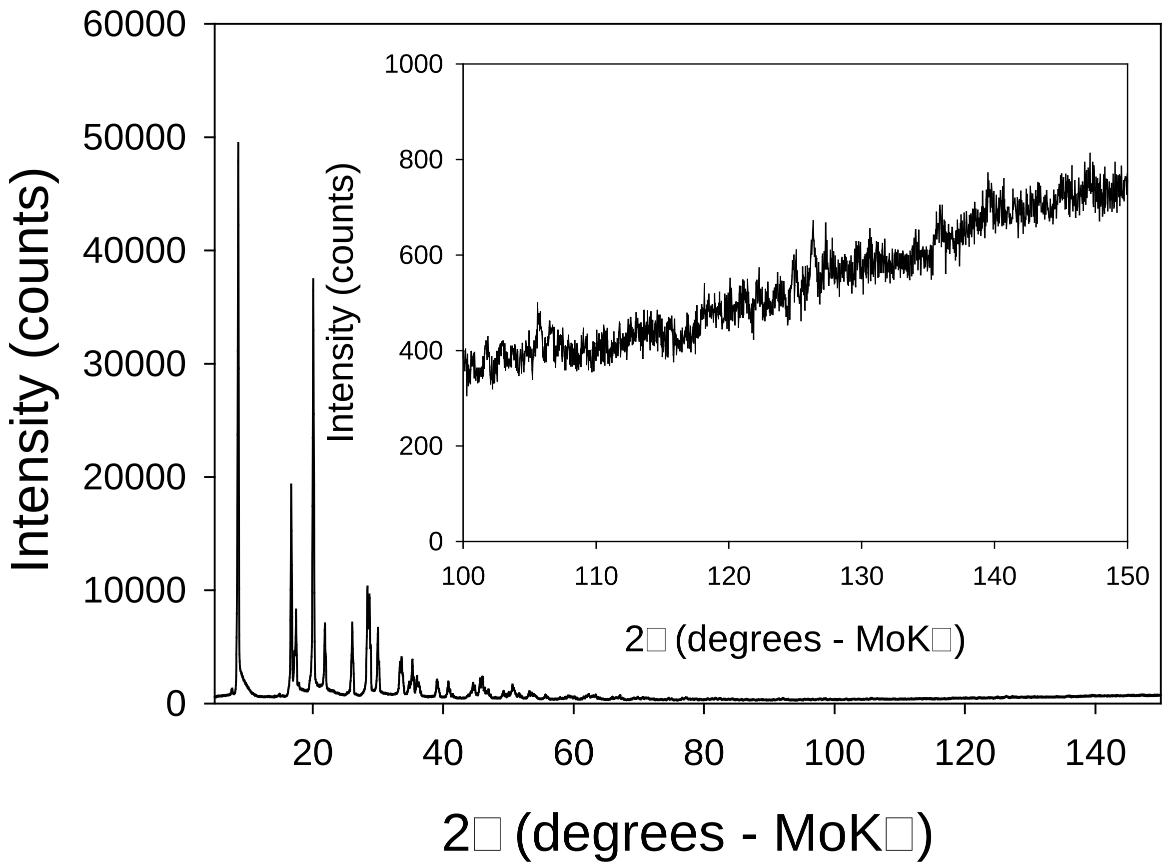
- Capillary geometry desirable
  - Monochromator versus mirror?

- Trade-off between

Higher Q	Ag	✓	Mo	✗
Tube power	Ag	✗	Mo	✓
PSD efficiency	Ag	✗	Mo	✓

Example - $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$

- MoKα with Vantec PSD (10° window)
  - Efficiency ~50% in use versus CuKα (N.B. higher tube power)



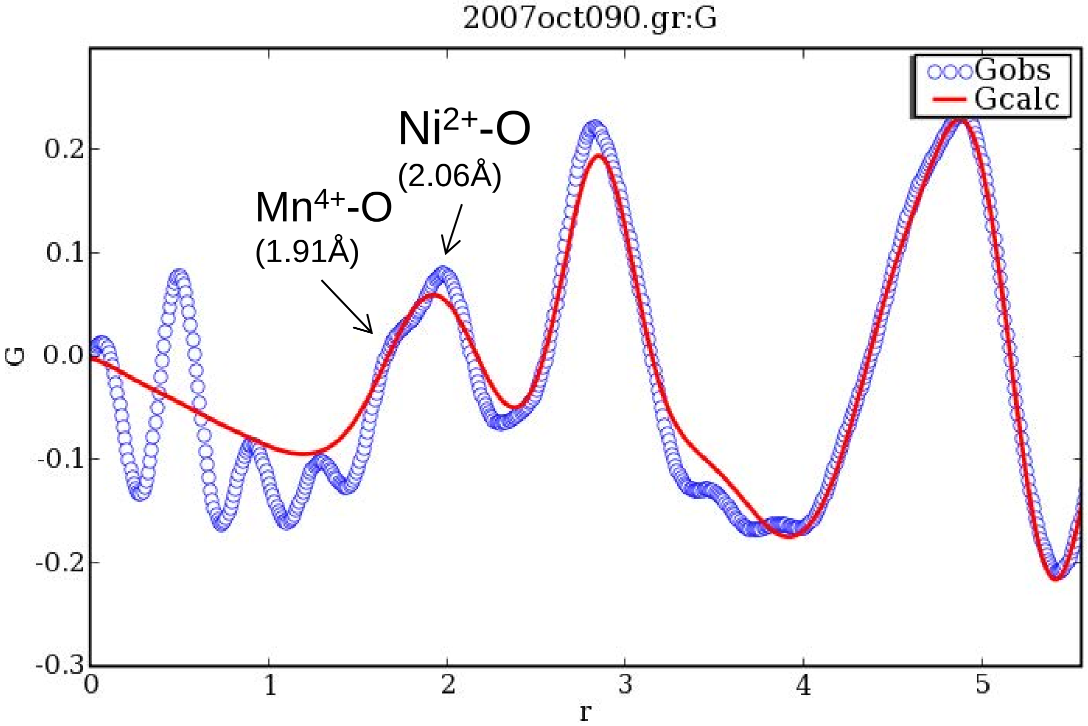
3 hour scan time (reflection)

Radial Soller slits to reduce background

40kV 55mA to minimize Xe escape peaks without primary optic (the ‘good’ Vantec)

$LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$

- PDFFIT just as happy with lab data
- Despite low resolution distortion away from average structure (red line) visible



Fit using PDFFIT of the average R-3m structure versus G(r)

Blowup shows the misfit in the TM-O environment

Conclusion

- Faster is not <u>always</u> better.....
- Counts aren't everything
  - less really can be more!

- Use best setup for the experiment, not the most expensive!
- In multi-user environments the single perfect instrument still doesn't exist
- Competing demands of speed, flexibility and accuracy lead to trade-offs

Gazing into the future?

- Better energy discrimination?
  - Hopefully…
- Better angular resolution?
  - Probably not….
- Is the future in the lab 2D?
  - For some but not all
- High energy
  - As above….

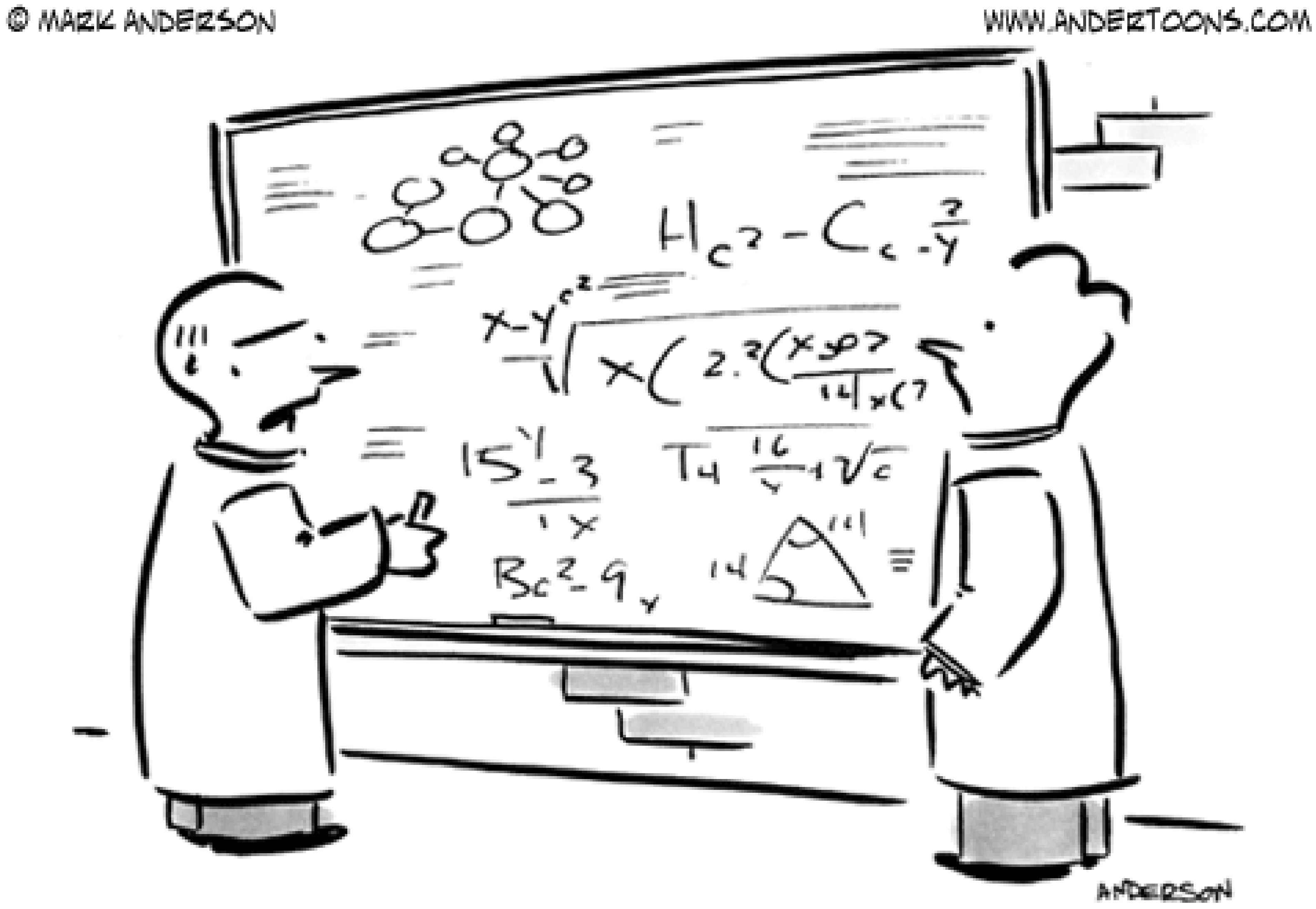
- Do the instrument vendors have more rabbits to pull from the hat?
  - Most certainly… ☺

NRC·CNRC

Acknowledgements…

- Ian Madsen
- Jim Cline

Questions…..?



"Screw Occam!"