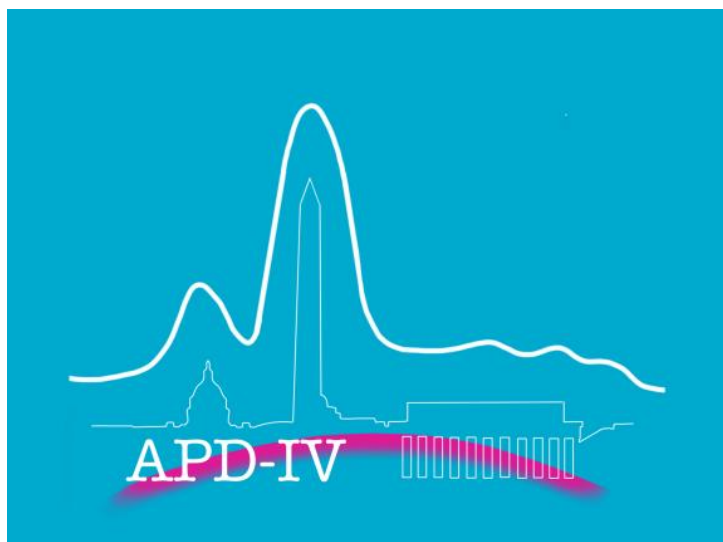


# ACCURACY IN POWDER DIFFRACTION IV

Critical parameters for  
instrument alignment and  
performance validation of XRD  
instrumentation

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# Introduction

- Accuracy in Powder Diffraction starts with accurate powder diffraction data
  - Also from laboratory instruments
- Did we get better in the last decade?
- Can we bring things further?

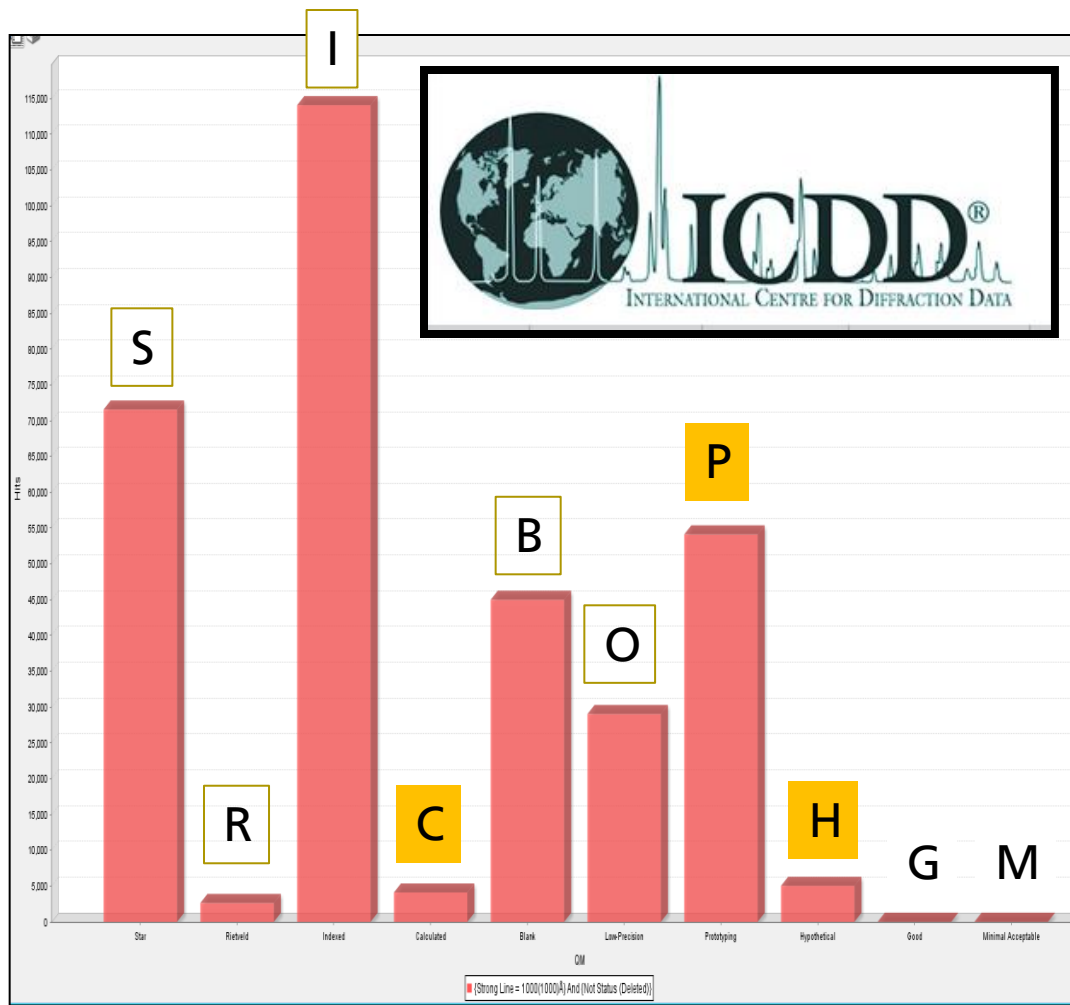
# Did we become better since 2001? (1)

PDF-4+  
Release 2013

Quality Marks  
Left to right

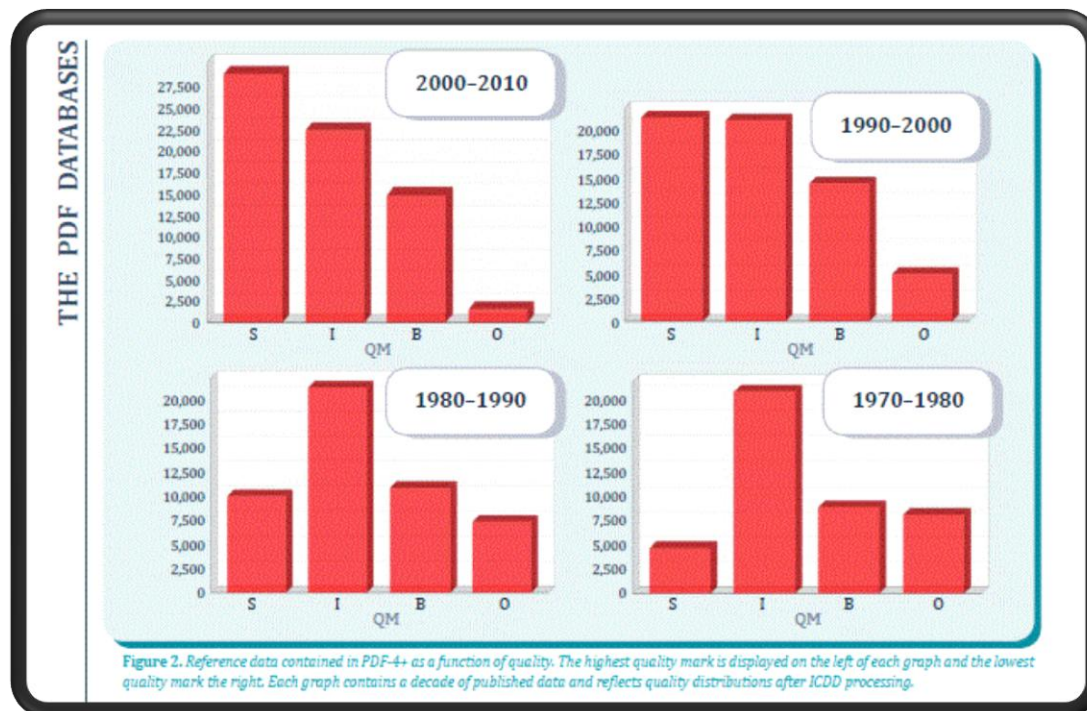
- Star
- Rietveld
- Indexed
- Calculated
- Blank
- Low-Precision
- Prototyping
- Hypothetical
- Good
- Minimal Acceptable

*Graphs made available by Dr. Timothy Fawcett, International Center for Diffraction Data*



## Did we become better since 2001? (2)

- More and more star patterns! Why?
- Better diffractometers
  - 1D detector
  - More use of monochromators and mirrors
- More use of higher-quality reference samples
- More use of software methods (Rietveld)



*The figure above was reproduced from the 2011-12 ICDD Product Catalog*

## What can a better diffractometer bring?

- Let us assume we have a small amount of organic powder



← 32 mm →

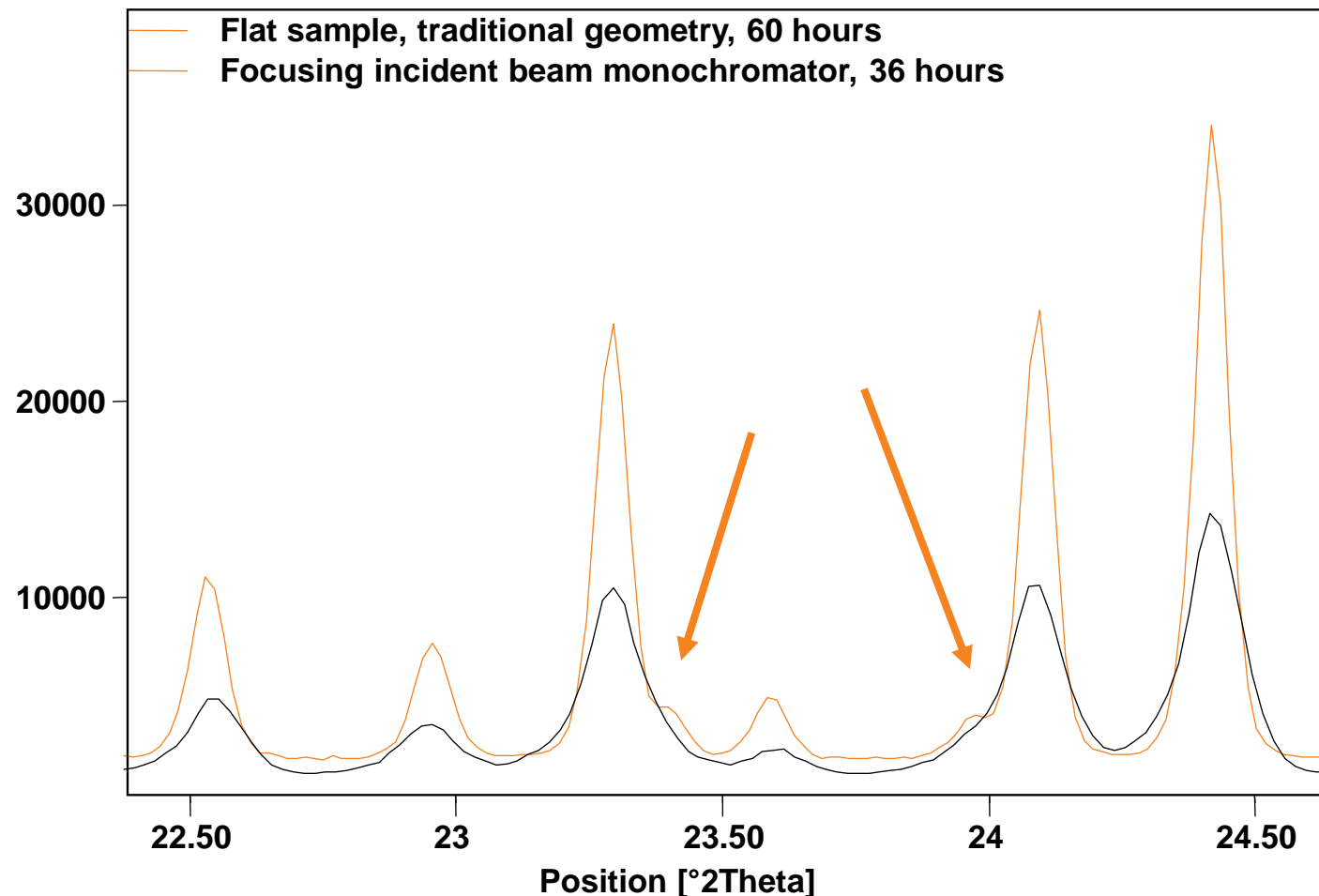
- Tetracycline Hydrochloride:
  - Sample 2 from the first SDPDRR in 1998 by A. le Bail and L. Cranswick - <http://www.cristal.org/SDPDRR/samples.html>

# What can a better diffractometer bring?

Parameter	15 years old geometry	Current geometry
Source	Cu LFF	Cu LFF
Divergence slit	10 mm, programmable	10 mm, programmable
Soller slits	0.04 rad	0.02 rad
Monochromator	Diffracted beam curved graphite	Primary beam Ge (Johansson)
Detector	0.3 mm receiving slit Xe-proportional counter (0D)	X'Celerator (1D)
Counting time	60 hours	36 hours

# What can a better diffractometer bring?

Counts



More resolving power in a shorter time frame....

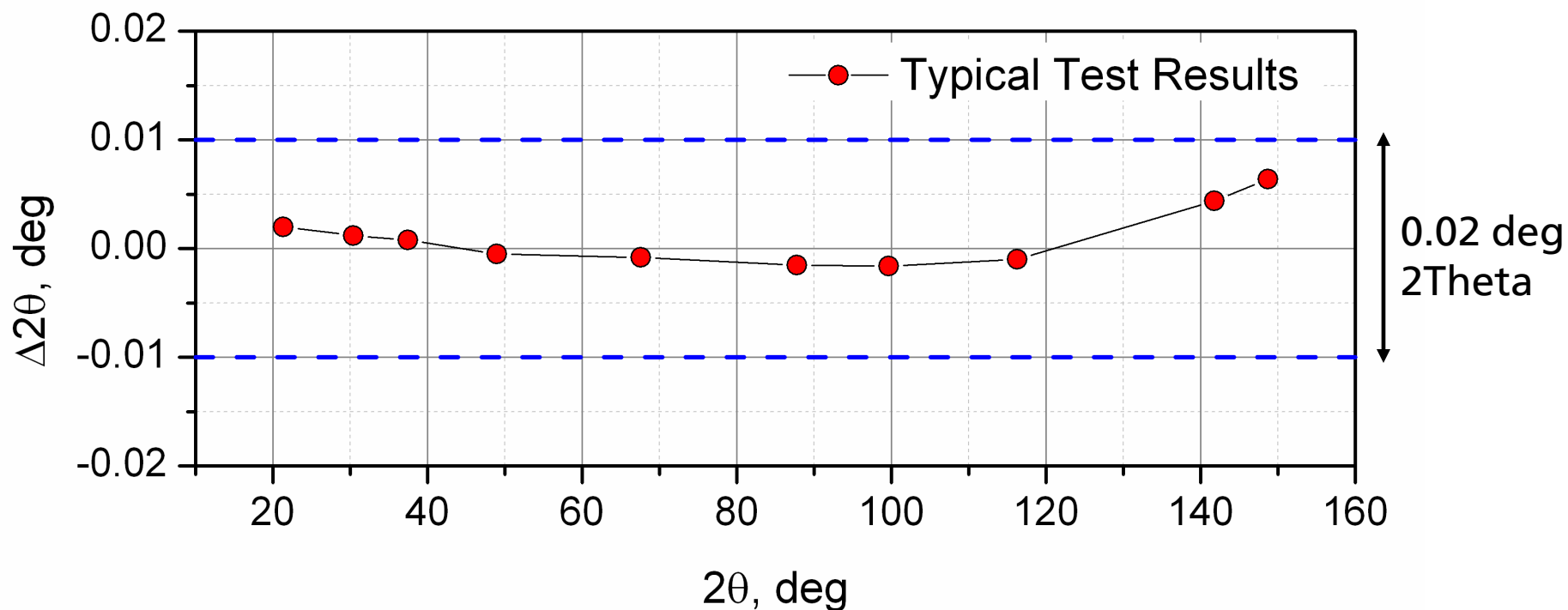
But can we also get better peak positions?

# How accurate can our peak positions be?

- Step 1: align instrument using optical methods
  - Direct beam position
  - Beam knives and slits
- Step 2: verify alignment with an appropriate sample
  - Take a material with well-known (=certified) lattice parameters
  - Measure a diffractogram over a large angular range, say from 20 to 160 deg 2Theta
  - Determine the positions of the peaks in the diffractogram
  - Plot the difference between the theoretical and experimental peak positions
  - The resulting bandwidth is an indication of the 2Theta linearity
- These measurements are done with the Bragg-Brentano reflection geometry



# 2Theta Linearity bandwidth graph

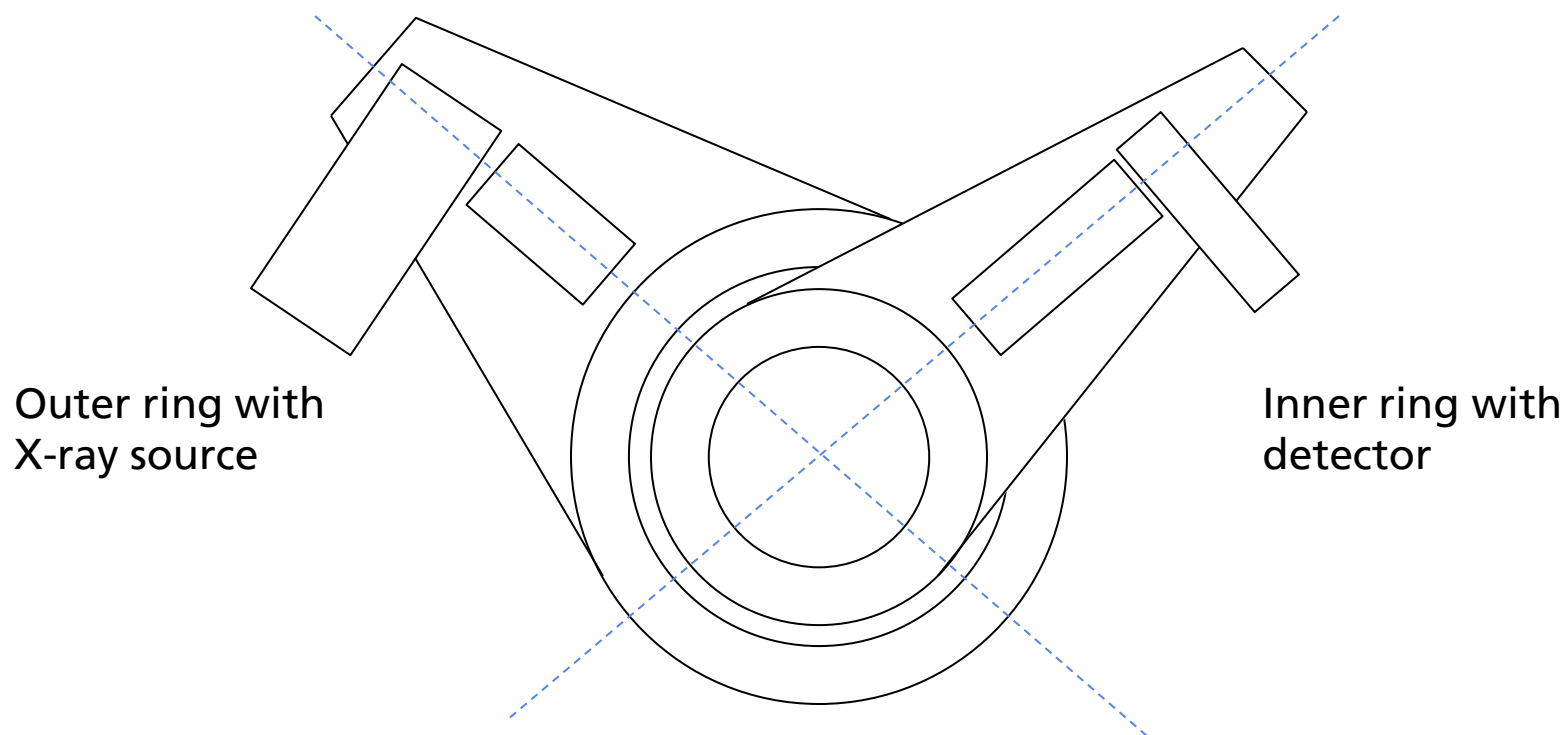


The sample: SRM660a LaB<sub>6</sub>

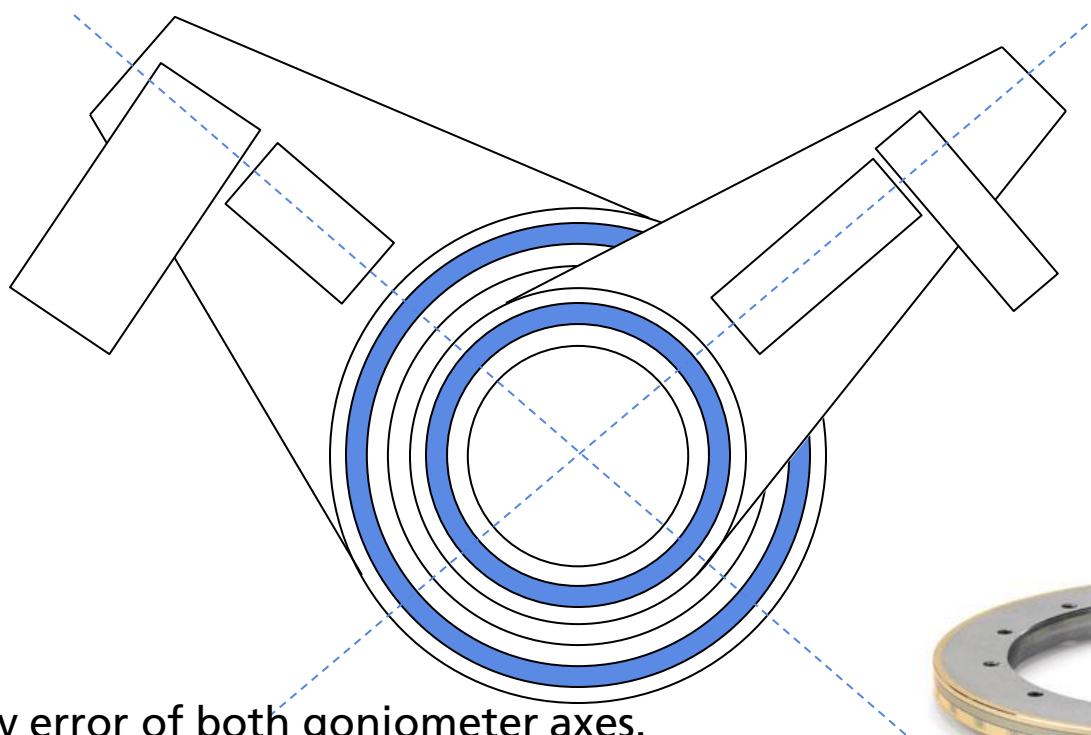
# Effects that contribute to the 2Theta linearity

Error	Contribution	Remarks
Goniometer linearity		
Gravity effects		
Optics reproducibility		
Non-flatness of sample		
Sample-to-holder error		
Holder-to-stage error		
Stage reproducibility		
Axial divergence		
Flat sample error		
Sample transparency		

# Goniometer linearity

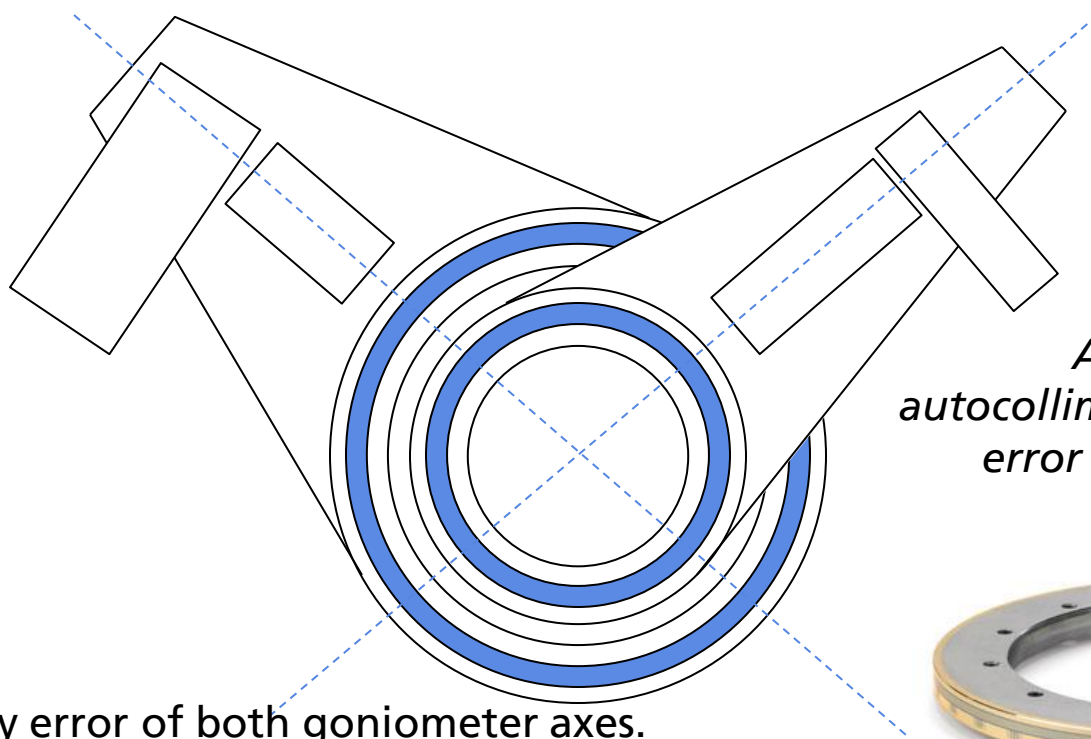


# Goniometer linearity



1. Concentricity error of both goniometer axes.
2. Measurement errors introduced by encoder ring (2x).
3. Alignment error (eccentricity) of encoder ring (2x).

# What does the goniometer bring?

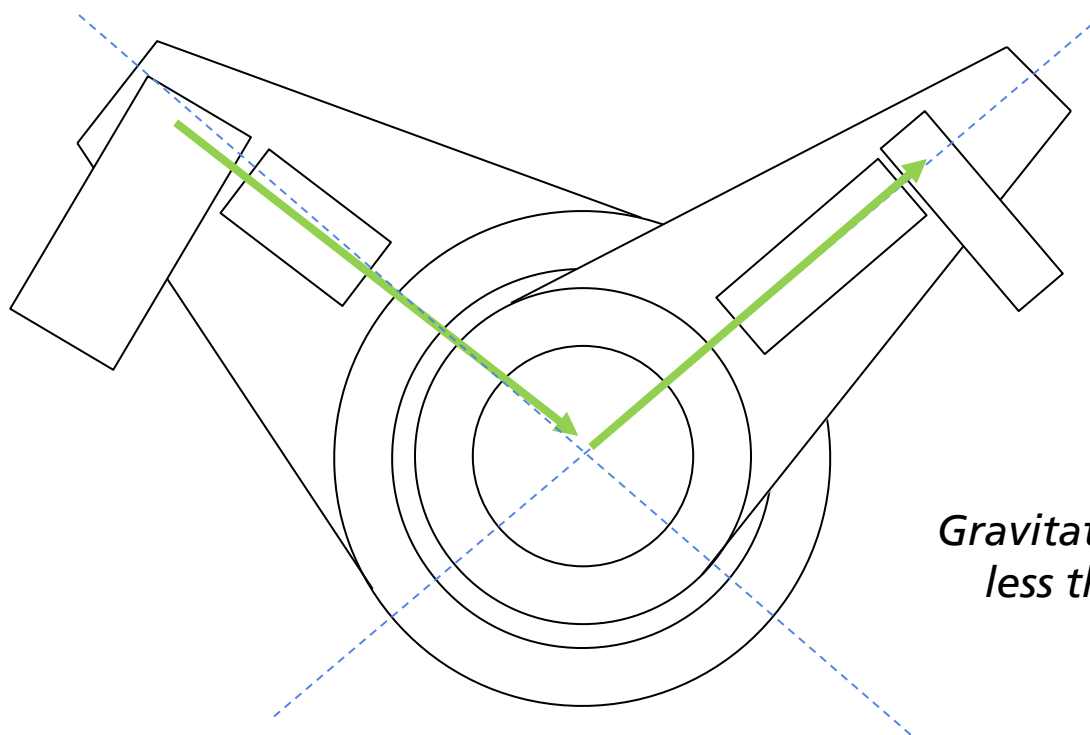


*As determined with an autocollimator, the goniometer error contribution is <math><0.002</math> degrees.*

1. Concentricity error of both goniometer axes.
2. Measurement errors introduced by encoder ring (2x).
3. Alignment error (eccentricity) of encoder ring (2x).



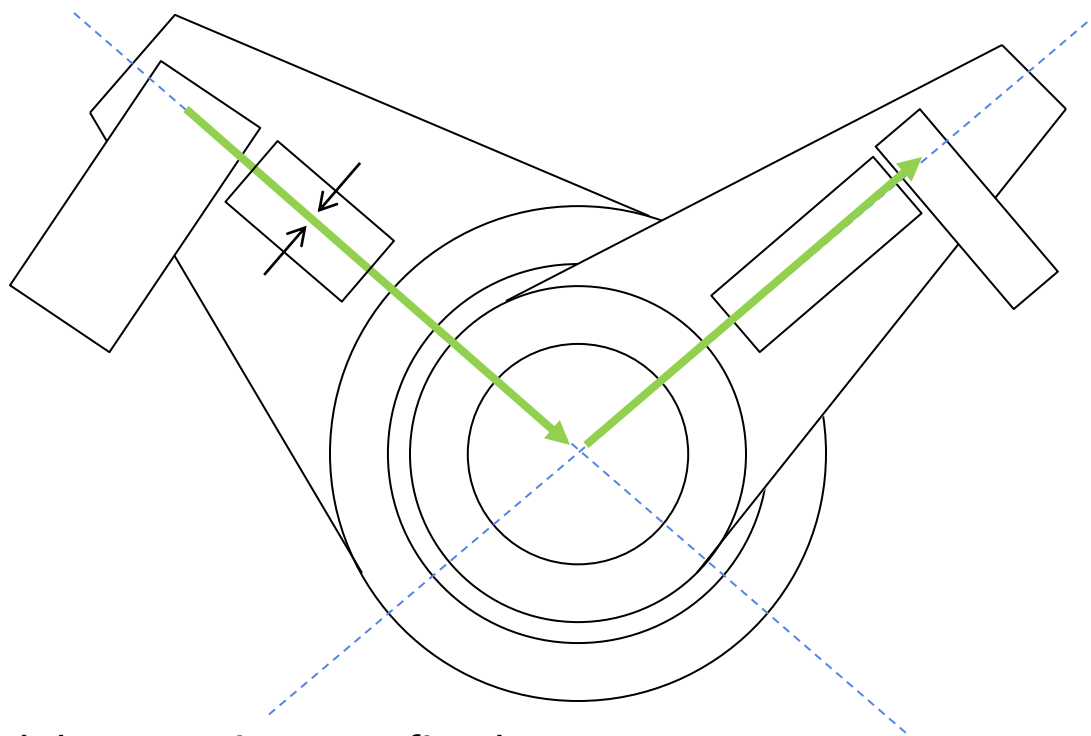
# The influence of gravity



*Gravitational errors should be less than goniometer errors (<0.002 degrees)*

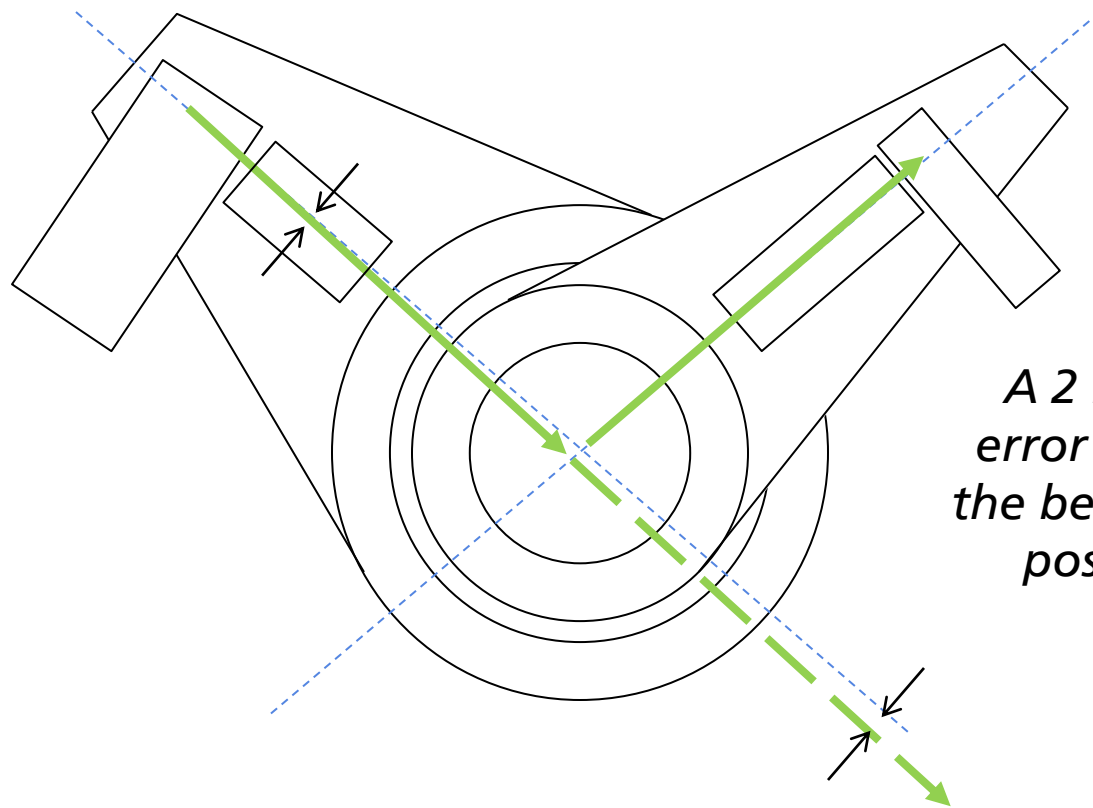
Gravitational effects are most prominent at low angles  
'Arm bending' will cause shifts of the beam

# Component errors (1): optical modules



In the 'good old days', optics were fixed  
Now people want to swap them for other components

# Component errors (1): optical modules

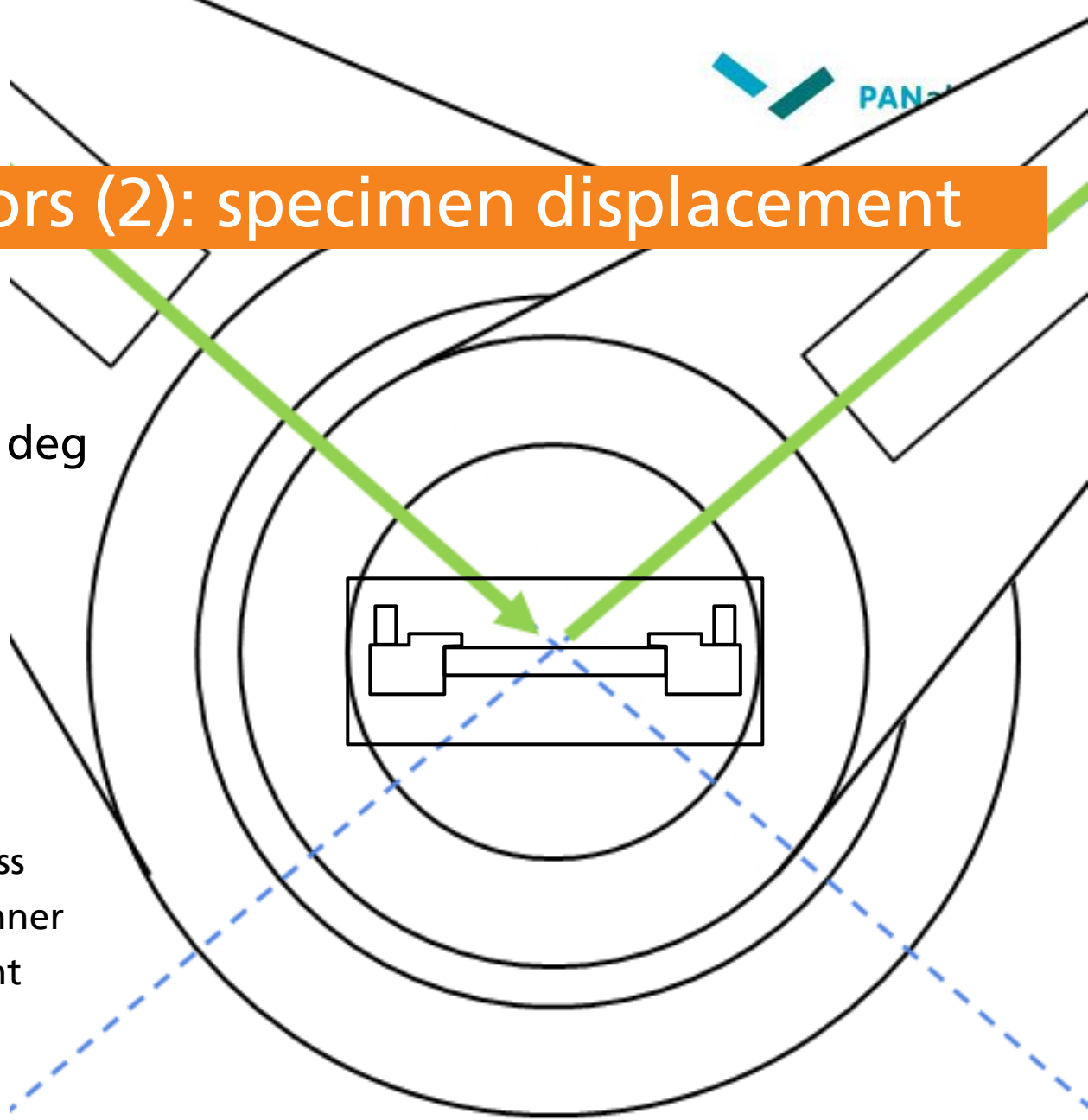


*A 2 micron positioning error results in a shift of the beam at the detector position of 12 micron: 0.0029 deg*

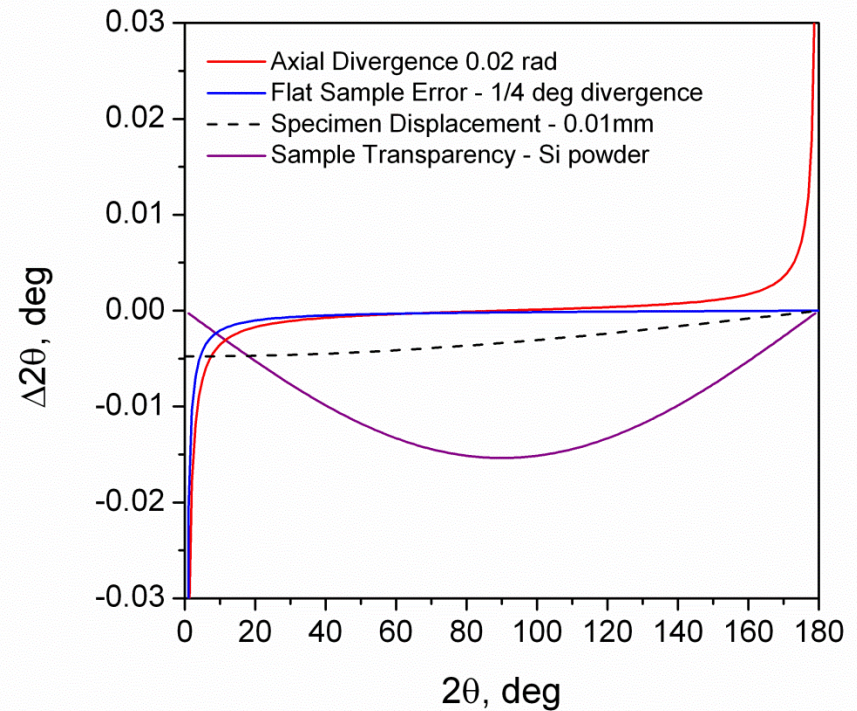
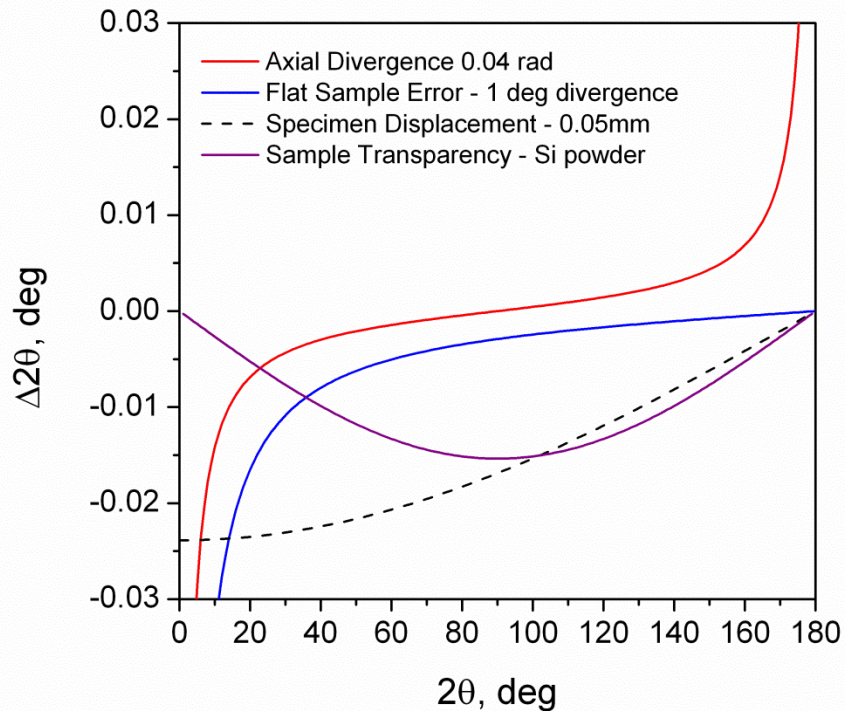


# Component errors (2): specimen displacement

- 10 micron sample displacement corresponds to 0.004 deg 2Theta at 40 deg 2Theta!
- In a Bragg-Brentano diffractometer this means:
  - Sample flatness
  - Sample holder flatness
  - Sample holder in spinner
  - Spinner on instrument
- $\ll 3$  micron each!



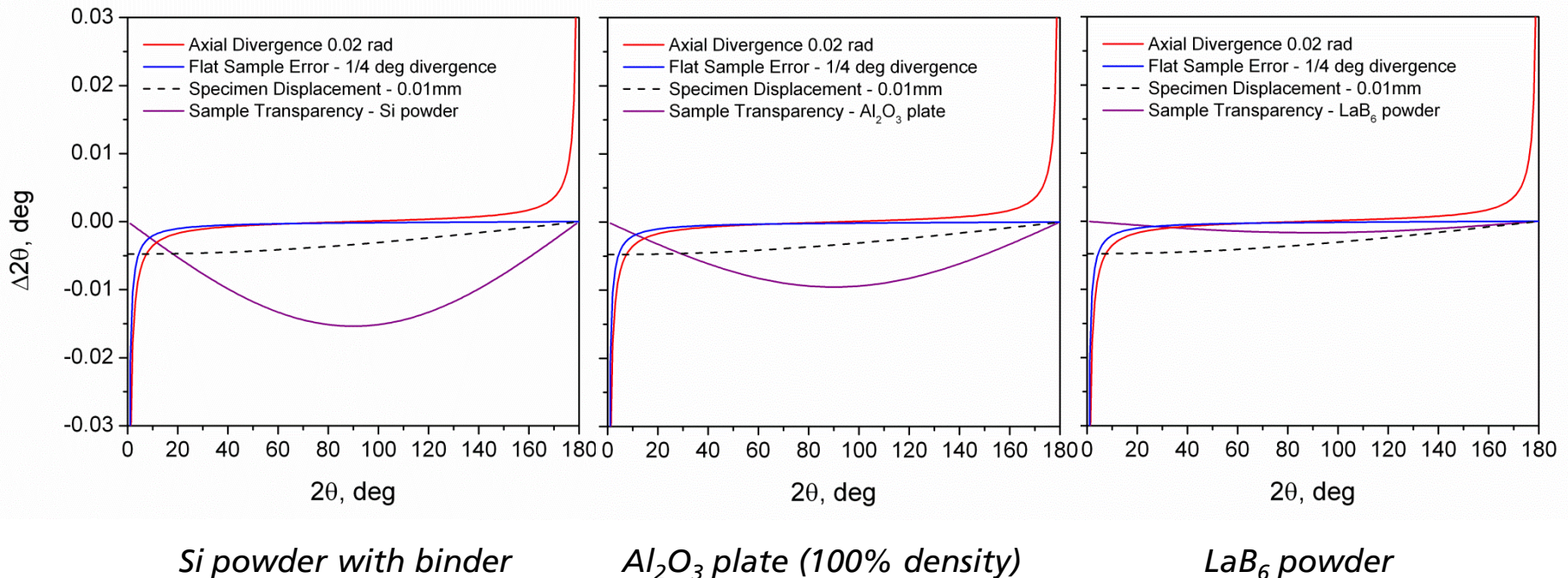
# Errors inherent to Bragg-Brentano geometry



*With a 1D detector, axial divergence and flat sample errors can be eliminated;  
Specimen displacement and sample transparency are more difficult!*

# The sample

- Sample displacement and sample curvature
  - < 3 micron (~0.002 deg 2Theta)
- Sample transparency should also be taken into account!



# What is the true peak position?

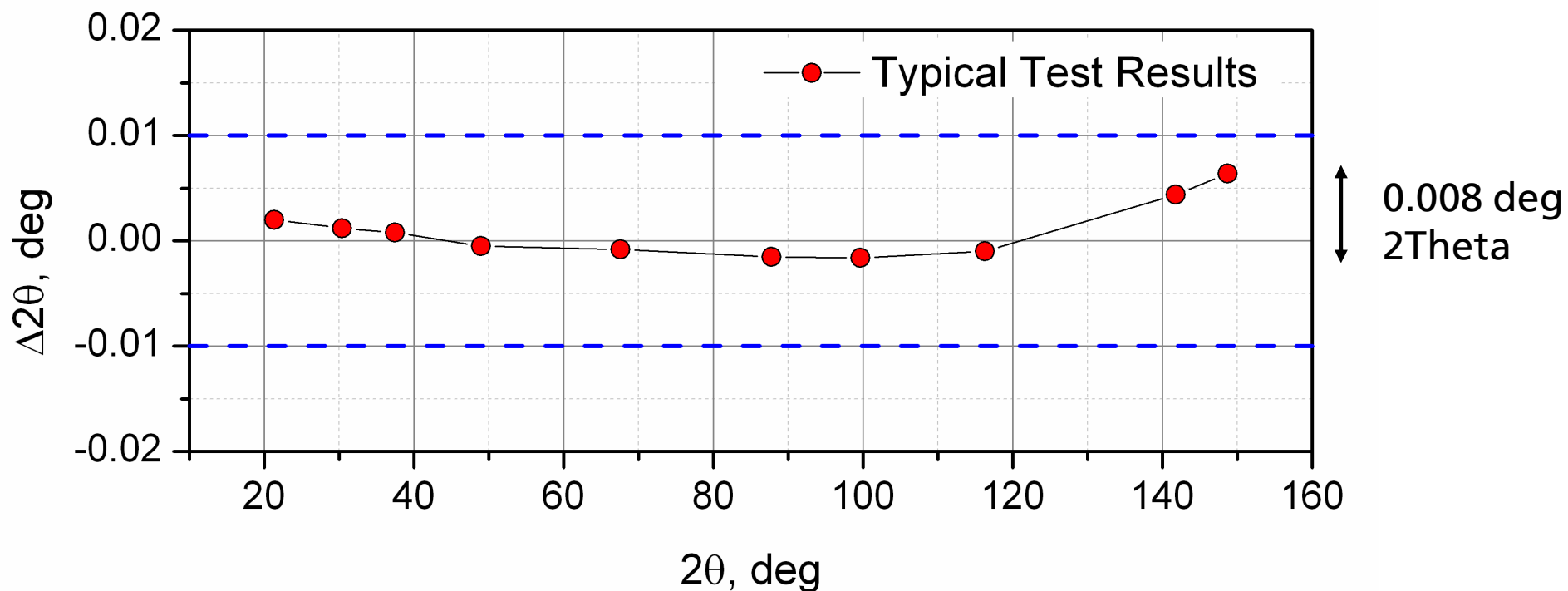
- Is it the...
  - Data point with highest intensity?
  - Top of smoothed peak?
  - Parabolic fit?
  - Full profile fits?
    - Which profile function?
- With narrow slits and Soller slits, as well as a sample with low transparency, the reflections become more symmetric, making the peak position determination less method-sensitive

# Effects that contribute to the 2Theta linearity

Error	Contribution	Remarks
Goniometer linearity	< 0.002 deg	Confirmed with autocoll.
Gravity effects	< 0.002 deg	To be further explored
Optics reproducibility	< 0.003 deg	~ 2 micron reproducibility
Non-flatness of sample	< 0.002 deg	~ 3 micron @ 40 deg 2Theta
Sample-to-holder error	< 0.002 deg	~ 3 micron @ 40 deg 2Theta
Holder-to-stage error	< 0.002 deg	~ 3 micron @ 40 deg 2Theta
Stage reproducibility	< 0.002 deg	~ 3 micron @ 40 deg 2Theta
Axial divergence	< 0.005 deg	With 0.02 rad Sollers
Flat sample error	< 0.001 deg	With ¼ deg divergence
<b>Sample transparency</b>	<b>&lt; 0.002 deg</b>	<b>Can be much higher!</b>

RMS: 0.008 deg

# 2Theta Linearity bandwidth graph



The sample: SRM660a LaB<sub>6</sub>

## So...

- We can break the 0.02 deg 2Theta barrier!
- But...
  - With a non-ideal sample (powder!)
  - With narrow slit settings (slow)
- How to prove this in the field?

## Field tests for 2Theta linearity

- Tests need to be fast and easy
  - Choose larger slit settings
  - Correct for positional shifts
- Sample has to be flat, solid and rugged
  - Correct for sample transparency
- Sample should also be useable for resolution tests
- Sample should be non-toxic, easy to ship worldwide and... cheap!



# Conclusions – instrument performance

- Instrumentation has improved over the last decade
  - 1D detector, also allowing the use of high-end optical modules
- The demand for multi-purpose instrumentation has added new elements in the equation
  - Alignment-free exchange of optics and sample stages requires repro of ~ 2-3 micron
- On a non-transparent sample, a 2Theta linearity < 0.01 deg 2Theta is nowadays possible
- We need the right sample for proving instrument performance

