Rietveld refinements collection strategies

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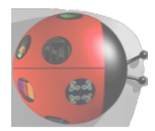
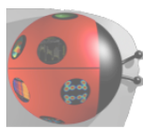


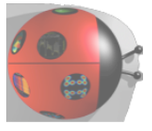
Quality of the experiment

- A good refinement, a successful analysis depends strongly on the quality of the experiment:
  - Instrument:
    - instrument characteristics and assessment
    - choice of instrument options
  - Collection strategies
    - range
    - step size
    - collection time
    - etc.
  - sample
    - sample size
    - sample preparation
    - sample condition



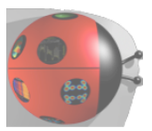
Instrument

- Rietveld refinements does not require at all the most powerful instrument but the one suitable for the analysis:
  - quantitative analyses of samples with big grain sizes (metal?, high crystal symmetries) require a diffracting volume of statistical significance => large sampling volume, large beam, with not too low divergence => a medium to low resolution diffractometer
  - structural refinements of low symmetries compounds (monoclinic, triclinic) require often a high resolution diffractometer
- Low and linear background is always preferred
- No additional lines (beta lines) is also in general preferred
- Large collectable ranges are important
- Higher diffraction intensities are also always good
- Smaller broadening help the analysis
- Simple geometries are better
- There is not the perfect instrument to get everything



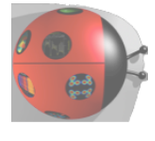
High resolution instruments

- These instruments put the emphasis on the smaller line width obtainable:
  - Pro:
    - less overlapped peaks (more details for structural refinements)
    - higher accuracy for microstructural analyses
    - better separation for multiple phases
    - smaller sampling volumes
    - higher cell determination accuracy
  - Cons:
    - smaller sampling volumes
    - low divergence (less grain statistic) => less accuracy in intensity
    - smaller intensities => higher collection times
    - more difficult to fit
    - more sensible to models
- Good for structural refinements when high precision is requested



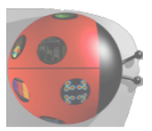
Low resolution instruments

- Pro:
  - higher intensities
  - better statistics (higher sampling volumes, more grains diffracting)
  - faster collection times
  - easier to fit
- Cons:
  - less details for complicated structures or samples
  - less precision (not always less accuracy)
  - not suitable for low symmetries compounds or determination of size-strain for highly crystallized samples
- These instruments are good for normal quantitative and qualitative analyses or when good statistic of grains is required (texture etc.).



A good overall instrument

- For quantitative analysis:
  - medium resolution
  - monochromator on the diffracted beam
  - Cu radiation ?
- Structural refinements or structure determination
  - high resolution
  - monochromator
  - no $K\alpha_2$ (structure determination)
- Microstructural analyses
  - high resolution
- Texture analyses
  - medium to low resolution
  - fast collection time
  - good statistic



Instrument assessment

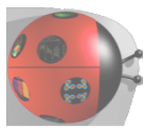
- In most cases (or always) the instrument alignment and setting is more important than the instrument itself

- Be paranoid on alignment, the beam should pass through the rotation center and hits the detector at zero 2θ

- The background should be linear, no strange bumps, no additional lines

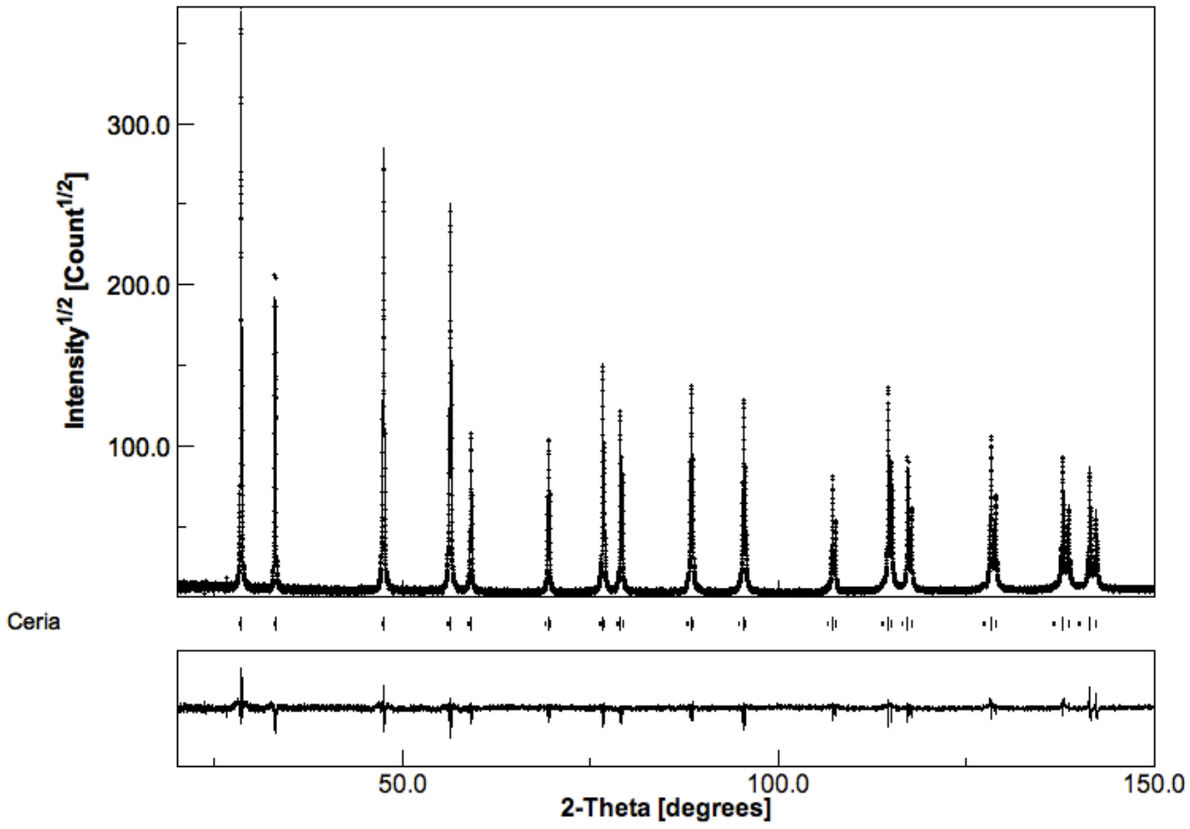
- Check the omega zero

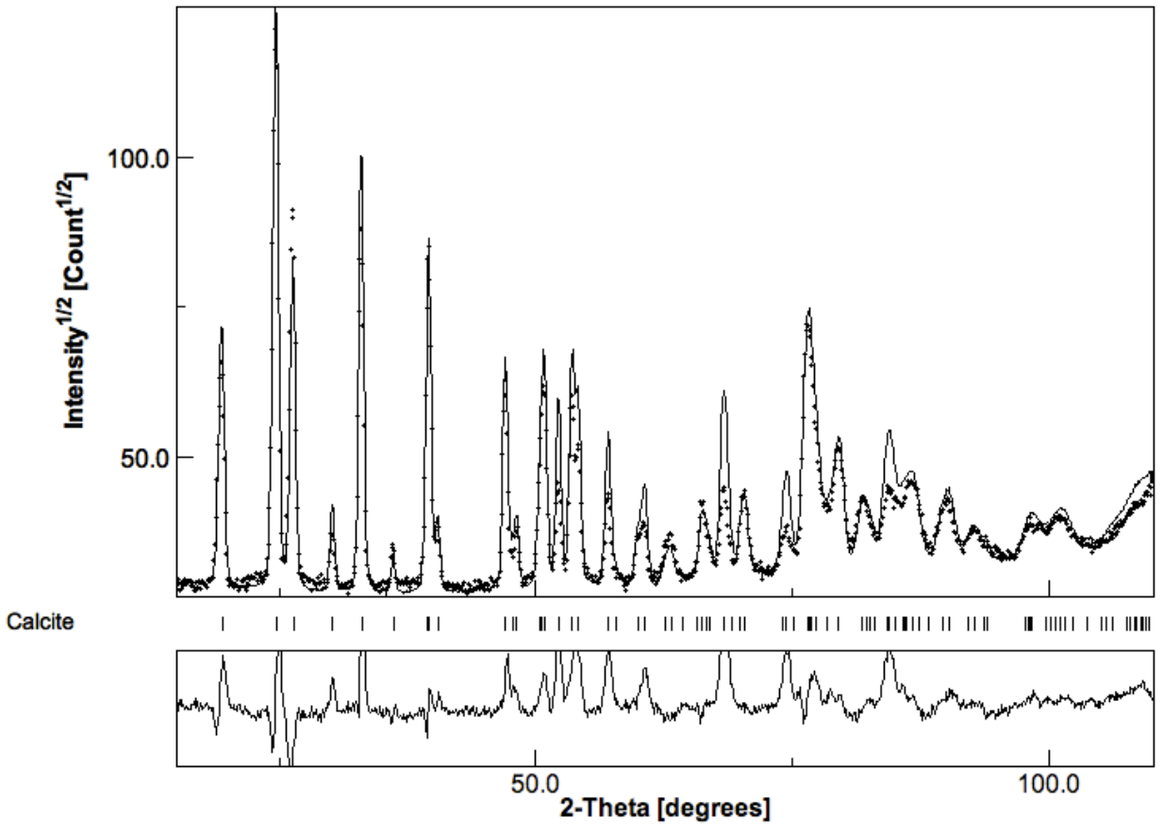
- Collect some times a standard for line positions and check if the positions are good both at low and high diffraction angle



The data collection

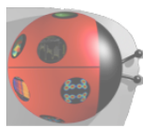
- The range should always the widest possible compatible with the instrument and collection time (no need to waste time is no reliable informations are coming from a certain range)





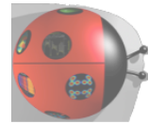
The step size

- The step size should be compatible with the line broadening characteristics and type of analysis
- In general 5-7 points in the half upper part of a peak are sufficient to define its shape.
- Slightly more points are preferred in case of overlapping.
- More for size-strain analysis.
- Too much points (too small step size) do not increase our resolution, accuracy or precision, but just increase the noise at equal total collection time
- The best solution is to use the higher step size possible that do not compromise the information we need.
- Normally highly broadened peaks => big step size => less noise as we can increase the collection time per step (> 0.05)
- very sharp peaks => small step size (from 0.02 to 0.05 for Bragg-Brentano)



Total collection time

- Ensure the noise is lower than the intensity of small peaks
- If the total collection time is limited, better a lower noise than a smaller step size.
- Better to collect a little bit more than to have to repeat an experiment.
- If collection time is a problem go for line or 2D detectors:
  - CPS 120: 2 to 5 minutes for a good spectrum of 120 degrees (good for quantitative analyses or follow reactions, transformations, analyses in temperature)
  - Image plate or CCDs: very fast collection times when texture is needed or is a problem
- Data quality (not related to intensity) of these detectors is a little bit lower than the one from good point detectors. But sometimes intensity rules!

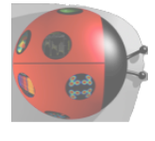


Respecting statistics

- In principle the measurement should be done at iso-statistical values:

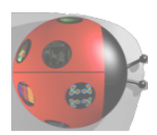
$$\frac{1}{\sqrt{I_i}}$$

- For practical reasons this is not always possible.
- Scattering factors and L-P effects decrease the intensity at high angle.
- In many cases, peaks at low angle are more sensible to heavy atoms and peaks at high angle to light atoms.
- A good strategy is to divide the range in different part and use a different collection time reducing the noise for the high angle part.

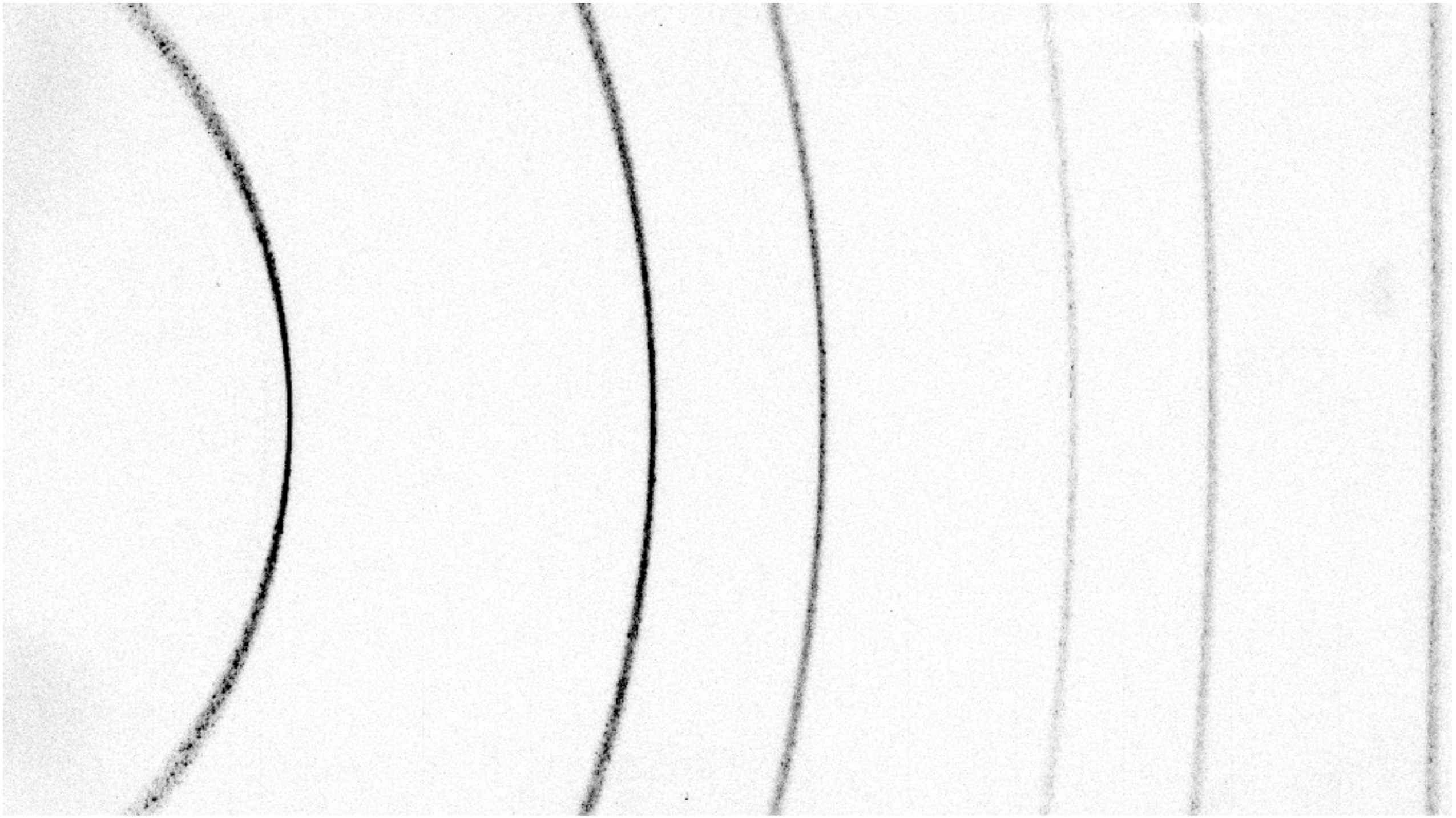


Sample characteristics

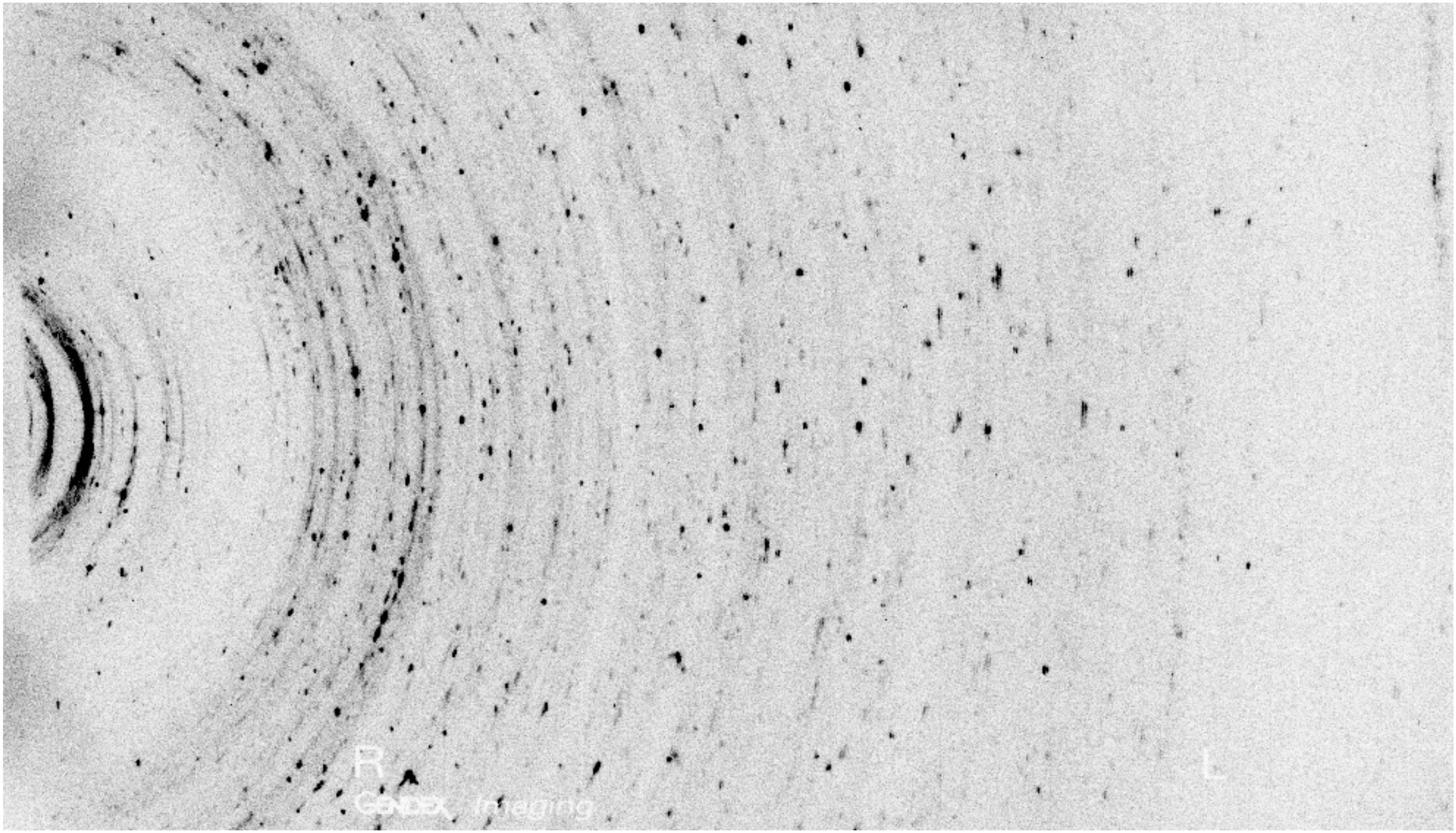
- The sample should be sufficiently large that the beam will be always entirely inside its volume/surface.
- Sample position is critical for good cell parameters (along with perfect alignment of the instrument).
- The number of diffracting grains at each position should be significant (> 1000 grains). Remember that only a fraction is in condition for the diffraction. Higher beam divergence or size increases this number. So the sample should have millions grains in the diffracting volume.



Grain statistics (sufficient)

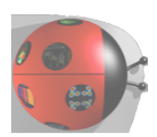


Grain statistics (poor)



Sample characteristics

- The sample should be sufficiently large that the beam will be entirely inside its volume/surface (always)
- Sample position is critical for good cell parameters (along with perfect alignment of the instrument)
- The number of diffracting grains at each position should be significant (> 1000 grains). Remember that only a fraction is in condition for the diffraction. Higher beam divergence or size increases this number.
- Unless a texture analysis is the goal, no preferred orientations should be present. Change sample preparation if necessary.
- The sample should be homogeneous.
- Be aware of absorption contrast problems
- In Bragg-Brentano geometry the thickness should be infinite respect to the absorption.
- Quality of the surface matters.



Ambient conditions

- In some cases constant ambient condition are important:
  - temperature for cell parameter determination or phase transitions
  - humidity for some organic compounds or pharmaceuticals
  - can your sample be damaged or modify by irradiation (normally Copper or not too highly energetic radiations are not)

- There are special attachments to control the ambient for sensitive compounds