STUDENTS

National Student Team Contest (first stage)
Solution of task 6. X-ray diffraction for the analysis of nanoparticles

1. The easiest equation to estimate the crystalline particle distribution using your experimental powder diffraction data is Scherrer equation. Applicability of the Scherrer equation could be limited the following constraints and restraints:

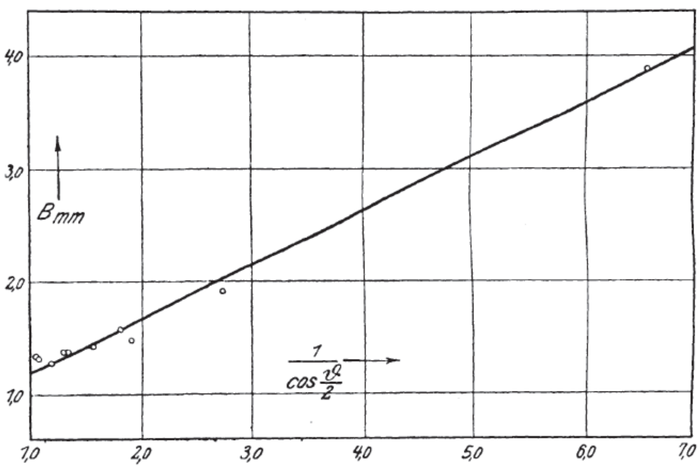
   - The peak broadening depends on equipment to be applied. Therefore, before the experiment the known model nanopowders of preliminary determined coherence length and crystallinity should be tested with the same diffractometer to reveal the instrumental broadening.
   - Asymmetry of reflection makes them inappropriate for Scherrer equation.
   - The overlapping reflections are not performed for crystallite size calculation using Scherrer equation.
   - Significant microstrain and disslocations are able to contribute to broadening of Bragg reflections equal to instrumental broadening.
     $B(2\theta) = 4\varepsilon \dfrac{\sin\theta}{\cos\theta}$ is the microstrain broadening where ε is the local strain.
   - Most of nanomaterials are nearly perfect because the particle size is smaller than size of dislocations or fracture, however temperature factor also take a part. Debye-Waller factor to be used to describe thermal vibrations, it should be estimated and correlate the reasonable result.

2. The Scherrer constant depends on shape of crystalline particles.

   According to Scherrer's results in 1918 the broadening parameter *B* is varied with θ as the following:

$$B = 2\sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\lambda}{L} \cdot \frac{1}{\cos\frac{\theta}{2}} + b \qquad (1)$$

   where θ is the diffraction angle, *L* is the rib length of polyhedron crystalllite, *b* is the characteristic lattice symmetry constant. The linear plot for the broadening parameter by Dr. Scherrer is given below. [1]



Nowadays, smaller values of Scherrer parameter (such as 0.89-0.96) are in use for coherence lengths estimation.

For example, the round shape nanoparticles of cubic symmetry (like metal gold and silver in Dr. Scherrer's experiments) corresponds to the K constant of about 0.9.

3. In his publication in 1918 Prof. Scherrer discussed XRD patterns of a series of inorganic nanocristallites, namely, colloidal precipitates of gold, silver and silicagel. For a comparison he analyzed three organic colloids including gelatin, starch, and cellulose.

   The XRD data were collected using a transmission geometry diffractometer and Cu K radiation. The corresponding β- and γ-lines were described by Scherrer as "less intensive" lines.

4. Gold nanoparticles should be smaller because of broader lines in diffractograms. Both metals have equivalent lattice constants and the same Fm3m space group and so the parameter *b* (Eq. 1) is to be similar for both the materials. Gold: 4.065(1) Å, Silver: 4.079(1) Å.

   Coherence length for gold nanoparticles in precipitate was estimated to be ~ 9 nm. For the silver sample L reached 16 nm approximately.

5. Reflection (200) is the most appropriate for analysis.

References:

[1] P. Scherrer, *Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen*, Nachr. Ges. Wiss. Göttingen. **26** (1918) 98-100.
[2] J. I. Langford and A. J. C. Wilson. *Scherrer after sixty years: a survey and some new results in the determination of crystallite size.* J. Appl. Cryst. **11** (1978) 102-113.