Uncertainty evaluation of crystallite size measurements of nanoparticle using X-Ray Diffraction analysis (XRD)

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Abstract. Crystallite size is one of the critical powder characteristics to determine nano-scale properties used in many industrial applications. The crystallite size can be extracted by X-ray Diffraction (XRD) analysis since it is one of the simplest and the most convenient method among numerous characterization techniques. However, the lack of suitable uncertainty evaluation for determining crystallite size makes the measurement questionable. Therefore, this paper has presented the uncertainty evaluation for crystallite size measurement based on the method of JCGM 100:2008. The main contributions according to the Scherrer equation consist of the Scherrer constant (K), the X-ray wave length (λ), the full width of the peak at half maximum intensity (FWHM), the diffraction angle (θ), and also the resolution and repeatability effect. The measurement process, statement of the standard uncertainty of the component sources, sensitivity coefficient and the combined standard uncertainty of crystallite size measurement have been explained in detail. A numerical example presents how to estimate the uncertainty budget for the nanoparticle of TiO₂ or P25 which is a commercially available powder.

1. Introduction
Crystallite size in nanoparticle is one of the critical characteristics in nanoscale technology. It plays an important role in nanoparticle to determine physical, chemical and other properties [1-2]. There are various methods for determining crystallite size such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD). However, XRD is one of the simplest and most common techniques for determining the crystallite size [3]. XRD analysis provides the broadening of diffraction peaks produced by the constructive interference of the scattered monochromatic X-ray at specific angle from each set of lattice planes in a sample [4]. Consequently, the diffraction peak broadening can be analyzed to estimate the average crystallite size of nanoparticles based on the mathematical model of Scherrer equation [5-7] which consists of Scherrer constant (K), the X-ray wave length (λ), the full width of the peak at half maximum intensity (FWHM), and the diffraction angle (θ).

This paper presents a thorough evaluation of the uncertainty for crystallite size measurement using XRD by considering all input values based on type A and type B uncertainty evaluation based on JCGM 100: 2008 [8].

2. Crystallite size measurements using XRD
X-ray diffractometer manufactured by Rigaku, model Miniflex, was employed in order to investigate the crystallite size of nanoparticle. The instrument is a benchtop X-ray diffractometer with advance detector (Hybrid pixel array detector) which enable high speed and low noise data collection. The results of broadening of the X-ray diffraction peaks were acquired and analyzed according to the Scherrer formula [5-7] in the “EVALUATION” environment. The crystallite size of TiO₂ powder (P25)
commercially available from the Sigma-Aldrich was investigated. Figure 1 illustrates XRD spectrum obtained after measuring P25 powder. The combination of rutile and anatase crystal structure was clearly observed. The diffraction peak at a position of 25 degree (2θ) was analyzed and the measurement result is summarized in table 1.

![X-Ray diffraction pattern of TiO2.](image)

**Figure 1.** X-Ray diffraction pattern of TiO2.

**Table 1.** The crystallite size measurement results of P25.

| No. | 2θ (degree) | Intensity | FWHM (degree) | Crystallite size (nm) |
|-----|-------------|-----------|---------------|----------------------|
| 1   | 25.309      | 13599     | 0.375         | 24.14                |
| 2   | 25.317      | 13303     | 0.379         | 23.88                |
| 3   | 25.306      | 13575     | 0.385         | 23.49                |
| 4   | 25.316      | 13424     | 0.373         | 24.23                |
| 5   | 25.322      | 13401     | 0.379         | 23.89                |
| 6   | 25.290      | 13599     | 0.363         | 24.90                |
| 7   | 25.296      | 13303     | 0.375         | 24.13                |
| 8   | 25.287      | 13575     | 0.379         | 23.85                |
| 9   | 25.295      | 13424     | 0.363         | 24.91                |
| 10  | 25.302      | 13401     | 0.376         | 24.07                |
|     | Average     | 25.304    | 13460.4       | 0.375                |
|     | SD          | 0.012     | 117.4         | 0.007                |

**3. Evaluation of standard uncertainty of XRD analysis**

In order to evaluate accuracy of the measurement result, one needs to know the uncertainty of the measurement. The uncertainty of crystallite size measurement was evaluated according to Type A and Type B uncertainty evaluation descripted in the JCGM100:2008 [8]. Type A evaluation can be applied as statistical analysis of series of observations. On the other hand, Type B is the method of evaluating the uncertainty by means other than the statistical analysis. It was noted that type A evaluation as the statistical analysis was determined with a pooled experimental standard deviation (SD) given the standard uncertainty as \( u_{Type\ A} = \pm \frac{SD(X)}{\sqrt{N}} \). For Type B evaluation, the denominator of the standard uncertainty (\( u \)) based on the types of probability distribution such as the rectangular and normal probability distribution were \( \sqrt{3} \) and 2 respectively.
In this case the evaluation of the standard uncertainty for crystallite size measurement using XRD method is based on a mathematical model of Scherrer equation. According to Scherrer equation, the crystallite size can be calculated from

\[ d = \frac{K \lambda}{\beta \cos \theta} \]  

where \( d \) is crystallite size (nm); \( K \) is Scherrer constant; \( \beta \) is the full width of the peak at half maximum intensity (FWHM); \( \lambda \) is the wavelength of X-ray (nm) and \( \theta \) is the diffraction angle.

3.1. The Scherrer constant (\( K \))

The Scherrer constant (\( K \)) is the characteristic property of the crystallite shape, such as at 0.94 for spherical crystals with cubic symmetry [5]. In case of P25, we examine particle shape of P25 using transmission electron microscope (TEM) and found that its shape is nearly spherical shape. However, since the particle shape and crystal shape may not be identical. The estimation of \( K \) value becomes source of uncertainty. We can estimate there are few scatter determination of \( K \) at approximately \( \pm 0.1 \). Therefore, the standard uncertainty due to Scherrer constant (\( u_K \)) with assuming rectangular probability distribution considered as type B uncertainty can be determined by

\[ u_K = \pm \frac{U_k}{\sqrt{3}} \]  

where \( U_k \) is the uncertainty due to the Scherrer constant.

3.2. Full width of the peak at half maximum intensity (FWHM, \( \beta \))

Diffraction peak profile is considered for determining the FWHM. FWHM is the width of the diffraction peak at a height half-way between background and the peak maximum. For obtaining these FWHM values from the diffraction pattern, it is necessary to separate the contribution of the instrument to the peak broadening (FWHM) from the contribution of the sample. The FWHM values of the latter are then used in the Scherrer formula to calculate an estimate for the crystallite size of the corresponding phase/compound. The program “EVALUATION” was used to fit curve the diffraction peak and estimated the FWHM. The uncertainty can be estimated by considering the standard deviation of FWHM on various measurements for different crystallite sizes. Therefore, the standard uncertainty due to FWHM (\( u_{FWHM} \)) with assuming normal probability distribution considered as type A uncertainty can be determined by

\[ u_{FWHM} = \pm \frac{SD \text{ of FWHM}(X_i)}{\sqrt{N}} \]  

where SD of FWHM (\( X_i \)) is the experiment standard deviation of FWHM of \( N \) number of measurements.

3.3. Wavelength of X-ray (\( \lambda \))

For XRD, it requires X-ray with wavelength in the order of the interatomic spacing to produce interference based on Bragg’s law, and hence the typical wavelength ranges are 0.07-0.2 nm [4]. The most common radiation used is Cu K\( \alpha \) at 0.15406 nm. To evaluate the uncertainty of wavelength, the value can be obtained according to the class of the X-ray source or directly from the calibration certificate of the X-ray source. In this case the calibration certificate provided by manufacturer indicates the uncertainty approximately 0.01 nm. Therefore, the standard uncertainty due to wavelength of X-ray (\( u_\lambda \)) with assuming normal probability distribution considered as Type B uncertainty can be determined by

\[ u_\lambda = \pm \frac{U_\lambda}{2} \]  

where \( U_\lambda \) is the uncertainty due to the wavelength of X-ray.
3.4. Diffraction angle (θ)
The diffraction angle is the angle between the incident beam and the normal to the reflecting lattice plane. Generally, the X-ray diffraction peak of the sample is operated over the 2θ range from 10 degrees up to 100 degrees at room temperature. The standard uncertainty can be estimated by considering the standard deviation of diffraction angle on repeated measurements. Therefore, the standard uncertainty due to diffraction angle \( u_\theta \) with assuming normal probability distribution considered as type A uncertainty can be determined by

\[
u_\theta = \pm \frac{\text{SD of } \theta (X_i)}{\sqrt{N}} \tag{5}
\]

where SD of θ \( (X_i) \) is the experiment standard deviation of diffraction angle \( (\theta) \) on \( N \) number of measurements.

3.5. Effect of angle step on XRD (Δθ)
There is a goniometer in XRD that either measure angle of detector or allows a sample to be rotated to a precise angular position. This XRD is operated at angle step of 0.01 degree. Therefore, the standard uncertainty due to the effect of angle step \( u_{\Delta \theta} \) with assuming rectangular probability distribution considered as type B uncertainty can be determined by

\[
u_{\Delta \theta} = \pm \frac{U_{\Delta \theta}}{\sqrt{3}} \tag{6}\]

where \( U_{\Delta \theta} \) is the angle step value used.

4. Calculation of the uncertainty for crystallite size measurements using XRD
In the case of the uncertainty of crystallite size measurement, these five parameters mentioned in previous section should be included in the estimation of the combined standard uncertainty, \( \mu(d) \):

\[
u^2(d) = C_K^2 u_K^2 + C_{FWHM}^2 u_{FWHM}^2 + C_\lambda^2 u_\lambda^2 + C_\theta^2 u_\theta^2 + C_{\Delta \theta}^2 u_{\Delta \theta}^2 \tag{7}\]

where \( C_i \) is the sensitivity coefficient associated with the input estimate \( X_i \) calculated by the partial derivative of the model function \( f \) with respect to \( X_i \).

Therefore, \( C_i \) for all factors here were presented as follow

\[
C_K = \left( \frac{\partial}{\partial K} \right) = \frac{\lambda}{K \cos(\theta)} \tag{8}
\]

\[
C_{FWHM} = \left( \frac{\partial}{\partial FWHM} \right) = \frac{K \lambda}{\cos(\theta)} \cdot \left( \frac{K}{\beta} \right) \tag{9}
\]

\[
C_\lambda = \left( \frac{\partial}{\partial \lambda} \right) = \frac{K}{\beta \cos(\theta)} \tag{10}
\]

\[
C_\theta = \left( \frac{\partial}{\partial \theta} \right) = \frac{K \lambda}{\cos(\theta)} \cdot \left( \frac{\sin(\theta)}{\cos(\theta)} \right) \tag{11}
\]

\[
C_{\Delta \theta} = C_\theta \tag{12}
\]

All contributions affect to the measurement uncertainty for the crystallite size determination from XRD technique were summarized in table 2.
Table 2. Uncertainty budget of crystallite size measurement of P25.

| Input Quantity                  | Unit   | Estimate | Standard uncertainty u(X_i) | Probability Distribution | Sensitivity coefficient, C_i | Uncertainty contribution u(Y_i) |
|---------------------------------|--------|----------|----------------------------|--------------------------|-------------------------------|---------------------------------|
| Scherrer constant, K           | -      | 0.900    | 0.0577                     | Rectangular              | 24.13                         | 1.393                           |
| Wave length, λ                  | nm     | 0.154    | 0.0050                     | Normal                   | 141.04                        | 0.705                           |
| FWHM, 2θ                       | rad    | 0.007    | 0.00004                    | Normal                   | -3321.37                      | -0.128                          |
| Diffraction angle, θ            | deg    | 12.652   | 0.0019                     | Normal                   | 4.88                          | 0.009                           |
| Angle step, Δθ                  | deg    | 0.010    | 0.00058                    | Rectangular              | 4.88                          | 0.028                           |
| Combined uncertainty, u_c       |        |          |                            |                          |                               | 1.567                           |
| Expended uncertainty, U_{95%}   |        |          |                            |                          |                               | 3.2                             |

In this case, the crystallite size of P25 is 24.2 nm ± 3.2 nm. The reported expanded uncertainty of measurement was stated as the standard uncertainty of measurement multiplied by the coverage factor \( k=2 \), which for a normal distribution corresponds to a coverage probability of approximately 95%.

5. Conclusion
Crystallite size is one of the primary characterizations for obtaining critical information of nanostructured materials. Crystallite size measurement can be usually carried out by X-ray diffraction reflection broadening by the Scherrer equation. The uncertainty evaluation of crystallite size measurement based on XRD technique was discussed in detail. The main source of uncertainty includes Scherrer constant used in calculation and wavelength broadening of the X-ray. When crystallite size of P25 was examined by using X-ray diffractometer manufactured by Rigaku, model Miniflex, expanded measurement uncertainty of 3.2 nm was obtained.

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