“Particle size measurement of standard reference particle candidates and theoretical estimation of uncertainty region”

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Key Words : Particle size, Standard reference particle,
Uncertainty region, Log-normal distribution, Size measurement,
Computer simulation

Abstract

In order to confirm reliable particle size measurement technique and to prepare standard reference particles for calibrating particle size measurement devices, experimental and theoretical studies have been conducted about particle size measurement of 0.1-1 μm silica particles.

The microscopic method with sample size greater than 90000 particles was conducted for the size measurement.

Theoretical equation of uncertainty region over all particle diameter range is newly proposed and compared with computer simulation. Previous paper (Masuda,H. and K.Iinoya;J.Chem.Eng.,Japan,4,60-67(1971)) reported the uncertainty region only for mass median diameter, but this paper presents the uncertainty region for all particle size range. The uncertainty region increases with the increase in particle diameter and also increases as the sample size decreases. Theoretical uncertainty region agreed with the results of computer simulation.

1. Introduction

Particle size distribution is measured by various methods such as microscopy method, laser diffraction and scattering method, dynamic light scattering method, electrical sensing zone method and liquid sedimentation method. Though the laser diffraction and scattering method, dynamic light scattering method and electrical sensing zone method have the advantage of shorter measurement time and good repeatability, but they need complicated calibration by direct method. In order to calibrate particle size measurement devices, it is necessary to prepare standard reference particles. For the reference particles, mono-disperse and poly-disperse particles are proposed. For the poly-disperse reference particles, Yoshida et al. measured particle size distribution of three kinds of spherical glass beads by use of improved type sedimentation balance and microscopic methods with sample size greater than 10000 particles (1,2). Mori et al. reported the results of the round robin test for the two kinds of particles (MBP1-10, 10-100) (3). This paper discusses the estimation method of uncertainty region for particle size distribution due to limited particle count number.

In order to represent particle size distribution by microscopic method, uncertainty region must be estimated. On this purpose, Masuda et al. derived analytical equation of the necessary sample size with known uncertainty region at mass median diameter (4). However, in order to know better information of particle size distribution by microscopic method, it is necessary to estimate uncertainty region over all the range of particle diameter.

In this report, particle size measurement of 0.1-1 μm silica particle was conducted. The microscopic method with sample size greater than 90000 particles was conducted for the measurement. Theoretical equation of uncertainty region over all particle diameter range is newly proposed and compared with computer simulation.

2 Microscopic method

Measurement of particle size distribution was carried out by use of silica particles produced by atomizing method of metal silicon solution under high temperature. Figure 1 shows a photograph of silica particles measured by scanning microscope (SEM S-4800, Hitachi, Co., Ltd.). The magnification and acceleration voltage were set to 20,000 and 2kV, respectively. In order to measure the length of particle size accurately, a certified scale shown in Figure 2 (MRS-4.1, Geller Microanalytical Laboratory, Boston) was used for the measurement. The scale attached in the SEM apparatus was not used and maximum deviation between the certified scale and the SEM scale was about 4%. For the microscopic method, the following procedure was used to prepare the sample plate.

(1) Acetone of 1 cm^3 and test silica particles of 0.001g was mixed in a glass beaker.

(2) Ultrasonication using bath (100W) about 1 hour was applied to the solution.

(3) Adhesive tape was attached on the surface of a highly oriented pyrolytic graphite base plate (HOPG, GRBS grade, NT-MDT, Rossia) and the surface was treated to change into hydrophilic surface.

(4) The slurry of 6 μ l was dropped on the tape and the plate was dried.

(5) The plate was inclined to 45 deg. and Pt coating was applied from two directions.

Figure 3 shows a photograph taken by SEM and each particle size was measured manually by marking a suitable sized circle on the particles. In order to eliminate counting error near the frames, size measurement was carried out only to the particles having the center positions inside the screen. Particle size measurement was not carried out for the non-spherical particles including strongly sintered or aggregated particles.

Figure 4 shows the change of particle size distributions for different sample size. As the sample size increases, the shape of size distribution tends to converge to a specific distribution. The total sample size is 93535 and size distribution curve tends to converge for sample size greater than about 20,000. It is found that particle size distribution ranges from 0.1 to 1.0 μ m.

Figure 5 shows the relation between mass median diameter and sample size. The mass median diameter approaches to about 0.34

μm as sample size increases, and the experimental results are indicated inside the calculated uncertainty region of the following equation. Assuming true particle size is represented by log-normal distribution with mass median diameter $x_{50,3}^*$ and geometric standard deviation σ_g, the mass median diameter obtained from sample size n indicates the following uncertainty region (3).

$$(1-\delta_1)\, x_{50,3}^* \le x_{50,3} \le (1+\delta_1)\, x_{50,3}^* \qquad (1)$$

Assuming 95% confidence level, the uncertainty region is as follows.

$$\delta_1 = 1.96\,\sigma \sqrt{\frac{36\,(1+18\,\sigma^2)}{n}} \qquad (2)$$

In the above equation, σ which equals to $\ln \sigma_g$ indicates the standard deviation. The uncertainty region increases with increasing the confidence level. The two lines shown in Fig.5 are the calculated values of the uncertainty region obtained by Eqs.(1),(2).

3 Estimation of uncertainty region over all particle size range

3-1 Uncertainty due to limited sample size

In order to obtain accurate particle size distribution, it is necessary to indicate uncertainty region over all particle size range. Assuming particle size distribution follows a log-normal distribution, the following equation is obtained to the mean particle diameter (4).

$$\bar{x}\,(m,\beta) = \left[\int_0^\infty x^m f^{(\beta)}(x)\,dx \right]^{\frac{1}{m}} = x_{50,\beta}\, \exp\,(\frac{m\,\sigma^2}{2}) \qquad (3)$$

For the size frequency distribution of $f^{(\beta)}(x)$, the parameter β equal to 0 and 3 means count and volume based distributions, respectively.

Let β equal to 0 in Eq.(3), the following equation is obtained.

$$\bar{x}\,(m,0) = x_{50,0}\, \exp\,(\frac{m\,\sigma^2}{2}) = x_{50,3}\, \exp\,(\frac{m}{2} - 3)\,\sigma^2 = \alpha\, x_{50,3} \qquad (4)$$

$$\alpha = \exp\,(\frac{m}{2} - 3)\,\sigma^2 \qquad (5)$$

The uncertainty region for a particle diameter at α times of mass median diameter is calculated by the following equation.

$$(1-\delta_1)\,\alpha\, x_{50,3}{}^{*} \le \alpha\, x_{50,3} \le (1+\delta_1)\,\alpha\, x_{50,3}{}^{*} \qquad (6)$$

$$\delta_1 = u\,\sigma \sqrt{\frac{m^2\,(1+0.5\,m^2\,\sigma^2)}{n}} \qquad (7)$$

The uncertainty region of the median diameter $\bar{x}(m,0)$ can be calculated by the Eqs.(6) and (7).

Uncertainty region for any particle diameter can be calculated from Eq.(6). For example, uncertainty regions for the following typical mean diameters can be calculated as follows.

(1) Mass median diameter, m=6, β =0

$$\alpha = 1 \qquad \delta_1 = u\,\sigma \sqrt{\frac{36\,(1+18\,\sigma^2)}{n}} \qquad (8)$$

(2) Mean volume diameter, m=3, β =0

$$\alpha = \exp\,(-1.5\,\sigma^2) \qquad \delta_1 = u\,\sigma \sqrt{\frac{9\,(1+4.5\,\sigma^2)}{n}} \qquad (9)$$

(3) Sauter diameter, m=5, β =0

$$\alpha = \exp\,(-0.5\,\sigma^2) \qquad \delta_1 = u\,\sigma \sqrt{\frac{25\,(1+12.5\,\sigma^2)}{n}} \qquad (10)$$

The parameter u is set to be 1.96 for 95% reliability.

3-2 Uncertainty due to microscopic measurement error

In order to measure accurate particle size, the certified scale shown in Fig.2 was used. However scale length measurement showed some uncertainty region. Figure 6 shows the relation between relative uncertainty value and scale length measurement. It is found that the relative uncertainty value increases as the scale length decreases.

3-3 Total uncertainty region

The total uncertainty region can be calculated by the following equation.

$$\sigma_e = \sqrt{{\sigma_1}^2 + {\sigma_2}^2} \quad (11)$$

$$\sigma_1 = \alpha \; x_{50,3} \, \delta_1 \quad (12)$$

$$\sigma_2 = x \, \delta_2 \quad (13)$$

where σ_1 and σ_2 are the uncertainty regions due to limited sample size and microscopic scale measurement, respectively. Figure 7 shows particle size distribution obtained by microscope with sample size 93535. The uncertainty region calculated by Eq.(11) is also shown in the Figure. Table 1 shows the uncertainty regions for various particle size ranges. For particle diameter greater than mass median diameter, the uncertainty region is mainly affected by limited sample size. The uncertainty region increases as particle diameter increases. This trend is clearly found for undersize greater than about 80%. When some large particles are included in the counting process, the volume fraction tends to move easily to larger particle side. Based on the counting process, the mass median diameter and geometric standard deviation obtained are as follows:

$x_{50,3} = 0.341\,\mu m$ $\sigma_g = 1.63$

Figure 8 shows the final particle size distribution indicated on log-normal distribution sheet. In this case, particle diameter ratio x/x_0 is used instead of particle diameter x. The reference diameter x_0 in this case is equal to $0.1\,\mu m$. It is found that particle size distribution follows to the log-normal distribution.

4 Computer simulation of uncertainty region over all particle size range.

Masuda et al.(5) examined the uncertainty region at mass median diameter by use of analytical solution and computer simulation. But this problem is not cleared except for the mass median diameter. The uncertainty region calculated by Eqs.(4)-(7) is an analytical solution and applied to the all particle size range. Then computer simulation is carried out to check the reliability of analytical solution. Figure 9 shows the calculated results compared with the analytical solution. It is assumed that true particle size distribution follows a log-normal distribution with $x_{50,3}$ of $0.341\,\mu m$ and σ_g of 1.63, respectively. In the simulation, random numbers that follow true log-normal distribution are used.

The sample size of one trial is 60000 and 500 trials are carried out. The dotted lines are the uncertainty region of analytical solution. It is found that simulation results are included inside the analytical solution. The simulation results are also indicated that the uncertainty region increases with particle diameter.

Figure.10 shows simulation results for trial number increased to 2500. The other conditions are the same as in Fig.9. Comparing Figs.9 and 10, simulated uncertainty region increases with trial number, but simulation results are included inside the analytical solution. Figure 11 shows simulation results with 2500 trials and sample size of one trial is 90000. Comparing Figs.10 and 11, the uncertainty region decreases as the sample size increases. Figure 12 shows simulation results with 2500 trials and the sample size in one trial is 120000. In this case, the uncertainty region decreases due to increased sample size. It is also found that uncertainty region increases as particle diameter increases. From Figs.9-12, the simulation results are within the analytical uncertainty region. These results have confirmed that the analytical solutions obtained by Eqs.(4)-(6) can be applicable to the estimation of uncertainty region over all particle size range.

Next simulations are carried out to check the criteria of end effect in log-normal distribution. Figure 13 shows simulation results as symbols and solid line indicates true particle size distribution. The closed circle shows simulation results with the particles within undersize from 1 to 99%. The open circle shows simulation results with the particles within undersize from 2 to 98%. The sample size is $2x10^5$. Deviations between true and simulated distributions are observed in the region of very small particle and large particle size. Figure 14 shows the same simulation results except for the sample size of $5x10^5$. Comparing Figs.13 and 14, it is found that, under the conditions examined, the end effect error becomes small as the sample size increases. It is found that deviation of size distribution due to end effect becomes small when the undersize from 1 to 99% is considered.

Conclusion

The uncertainty region of particle size distribution over all particle size range is examined and the following conclusions are obtained.

(1) The uncertainty region by the theoretical solution agreed with the numerical simulation.

(2) The uncertainty region increases with the increase in particle diameter. This trend is clearly found for undersize greater than about 80%.

(3) The uncertainty region decreases with the increase in sample size.

(4) For the undersize from 1 to 99% range, deviation of size distribution between true and truncated size distributions becomes small.

Nomenclature

$f^{(\beta)}(x)$: size frequency distribution of parameter β (-/μm)

m, β : parameter used in Eq.(3) (-)

n : sample size (-)

u : reliability parameter (-)

x, x_0 : particle diameter and reference particle diameter (μm)

$x_{50,3}$, $x_{50,3}^*$: mass median diameter and true mass median diameter, respectively (μm)

$\bar{x}(m,\beta)$: mean particle diameter defined by Eq.(3) (μm)

α : parameter used in Eq.(4) (-)

σ, σ_g : standard deviation of log-normal distribution and geometric standard deviation, respectively (-)

σ_1 : uncertainty region due to limited sample size (μm)

σ_2: uncertainty region due to scale length measurement (μm)

σe : total uncertainty region defined by Eq.(11) (μm)

δ_1 : uncertainty region due to limited sample size (-)

δ_2: uncertainty region due to scale length measurement (-)

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Figure Caption

Tab.1 Uncertainty region for various particle size range
Fig.1 Photograph of silica particles (SEM)
Fig.2 Certified –scale for SEM measurement
Fig.3 Photograph of silica particles by SEM
Fig.4 Particle size distribution for various sample size (20000—93535)
Fig.5 Mass median diameter for different sample size
Fig.6 Uncertainty region of scale measurement
Fig..7 Particle size distribution with uncertainty region
Fig.8 Particle size distribution indicated on log-normal sheet
Fig.9 Simulation results of uncertainty region (500 trials)
Fig.10 Simulation results of uncertainty region (2500 trials)
Fig.11 Simulation results of uncertainty region (n=90000)
Fig.12 Simulation results of uncertainty region (n=120000)
Fig.13 Simulation results of size distribution by selecting upper and lower size rang (n=200000)
Fig.14 Simulation results of size distribution by selecting upper and lower size rang (n=500000)

Table 1 Uncertainty region for various particle size range

Dp[μm]	α[-]	m[-]	δ_1[-]	σ_1[μm]	δ_2[-]	σ_2[μm]	σ_e[μm]
0.188	0.551	1	0.003	0.001	0.020	0.004	0.004
0.212	0.621	2	0.008	0.002	0.020	0.004	0.004
0.239	0.700	3	0.014	0.003	0.019	0.005	0.006
0.303	0.888	5	0.031	0.009	0.019	0.006	0.011
0.341	1.000	6	0.043	0.015	0.019	0.006	0.016
0.433	1.269	8	0.074	0.032	0.018	0.008	0.033
0.549	1.610	10	0.113	0.062	0.017	0.009	0.063
0.697	2.043	12	0.160	0.112	0.016	0.011	0.112

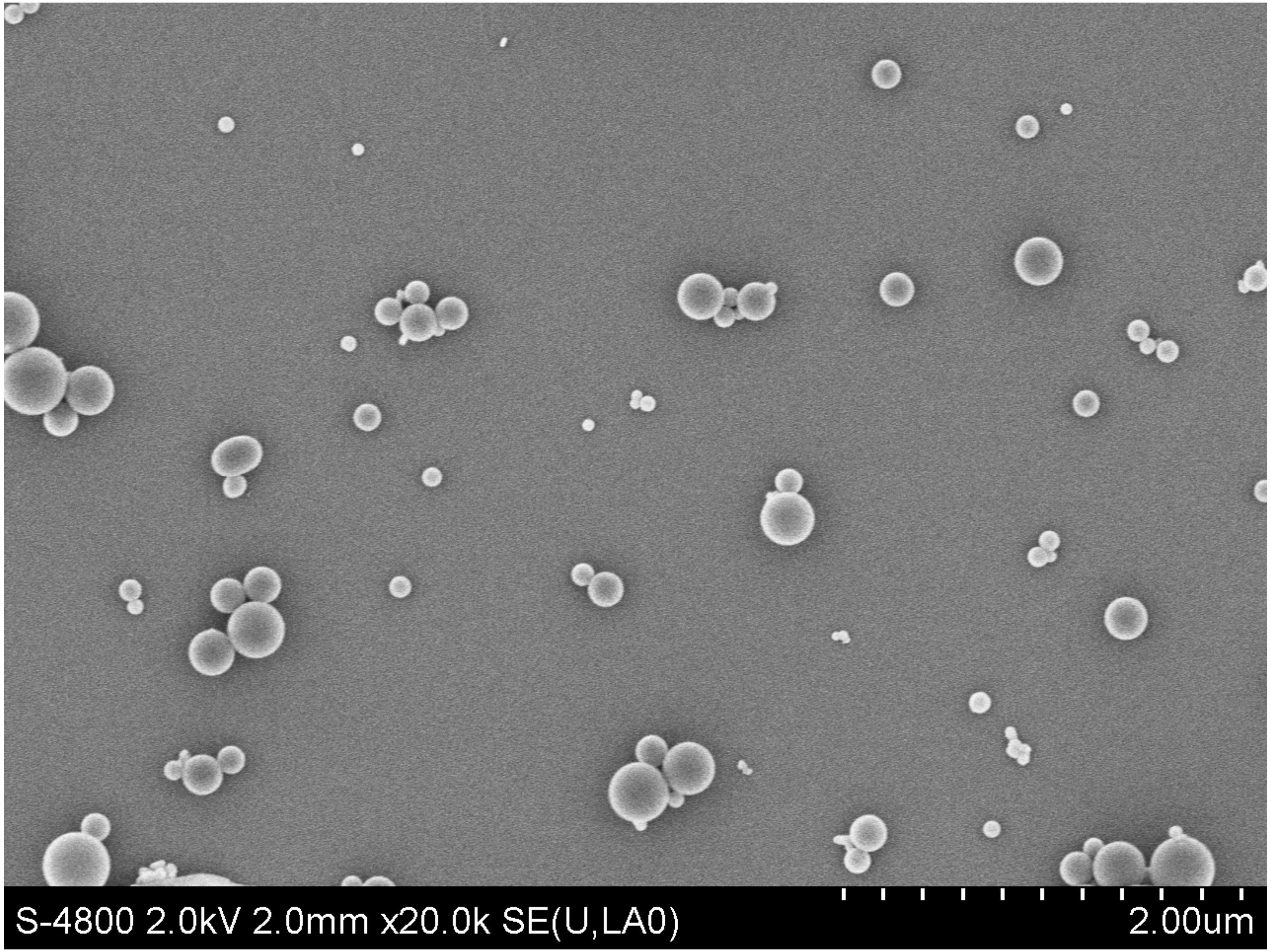

Fig.1 Photograph of silica particles (SEM)

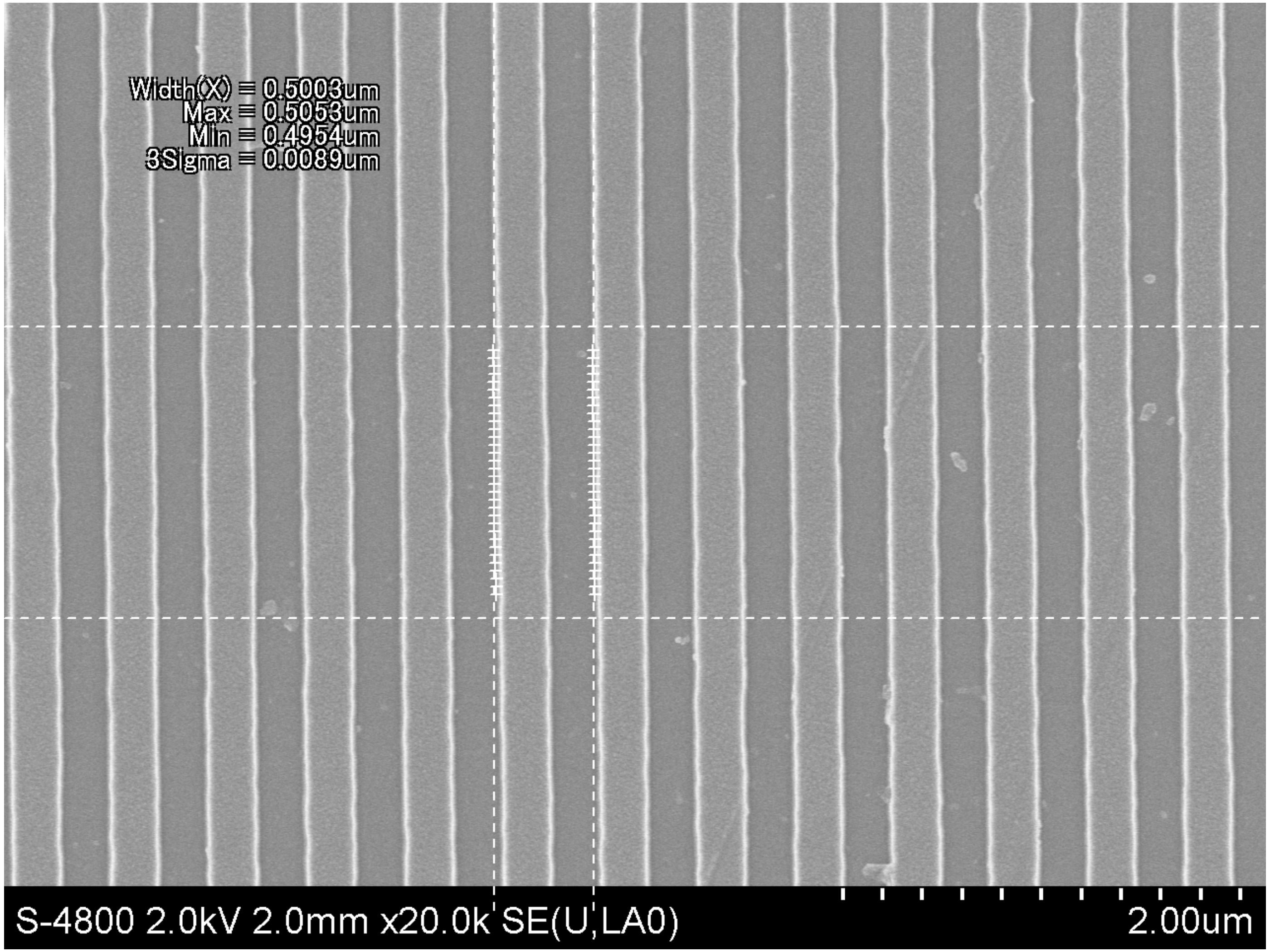

Fig. 2 Certified-scale for SEM measurement

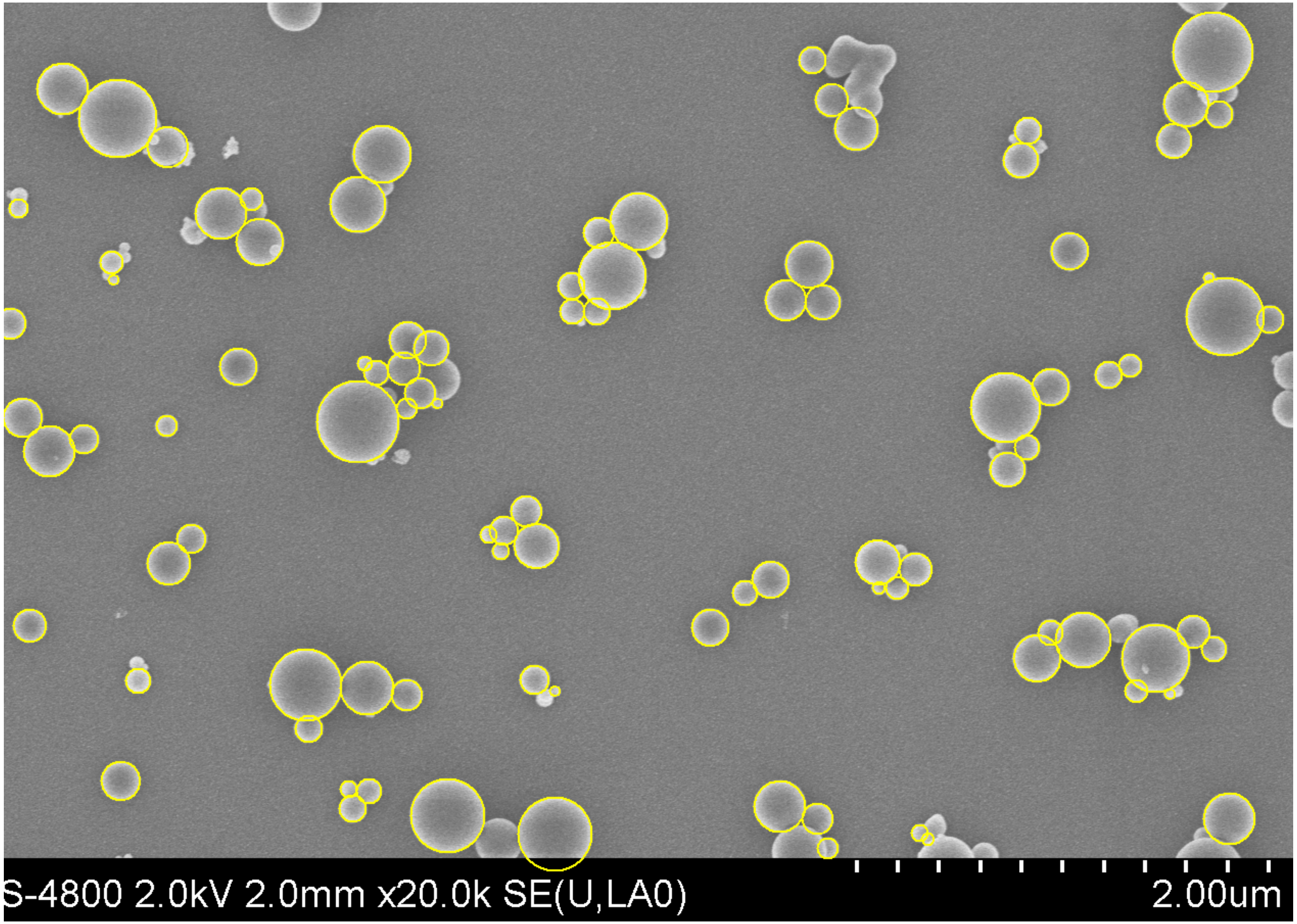

Fig.3 Photograph of silica particle by SEM

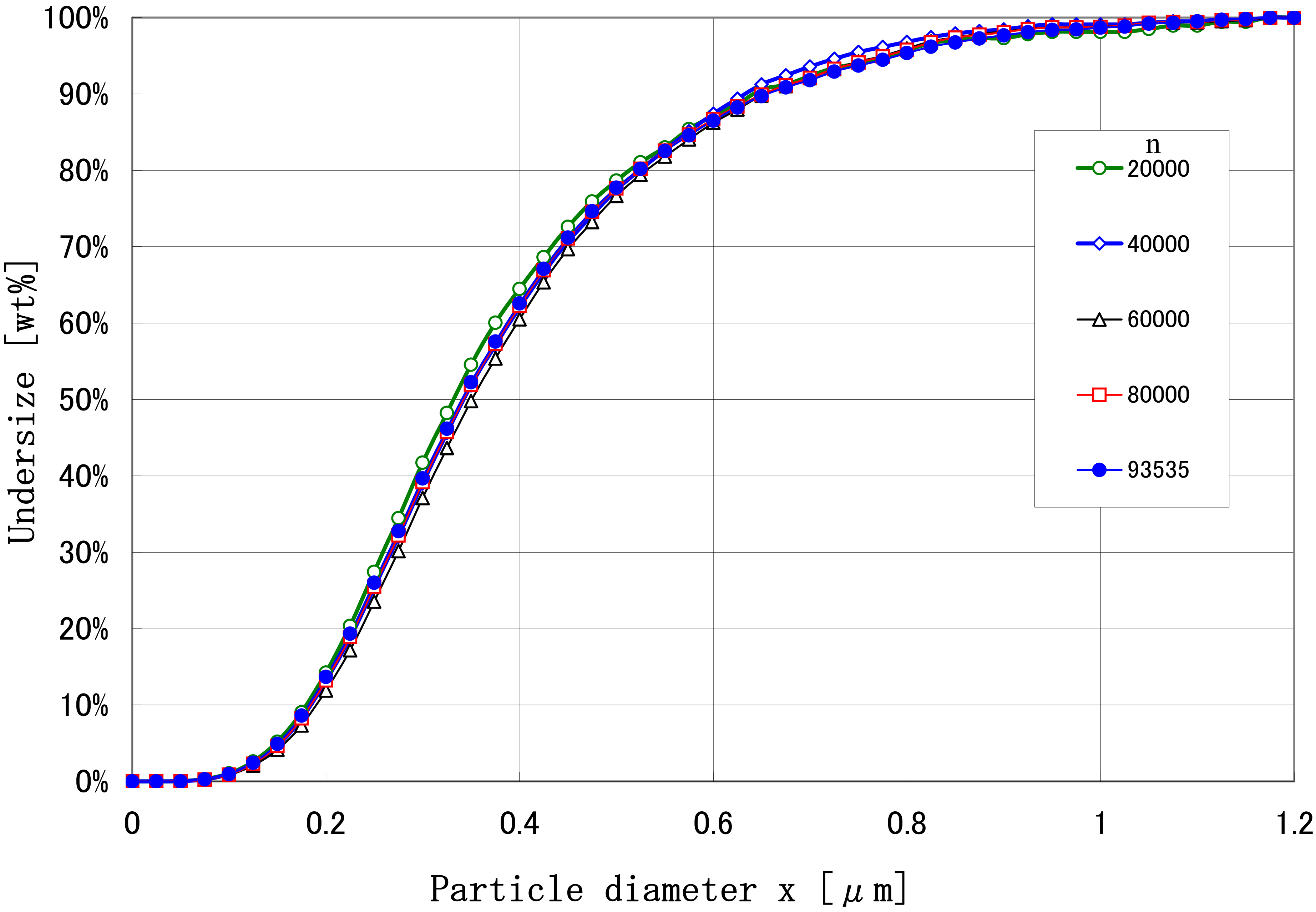

Fig.4 Particle size distribution for various sample size (5000～93535)

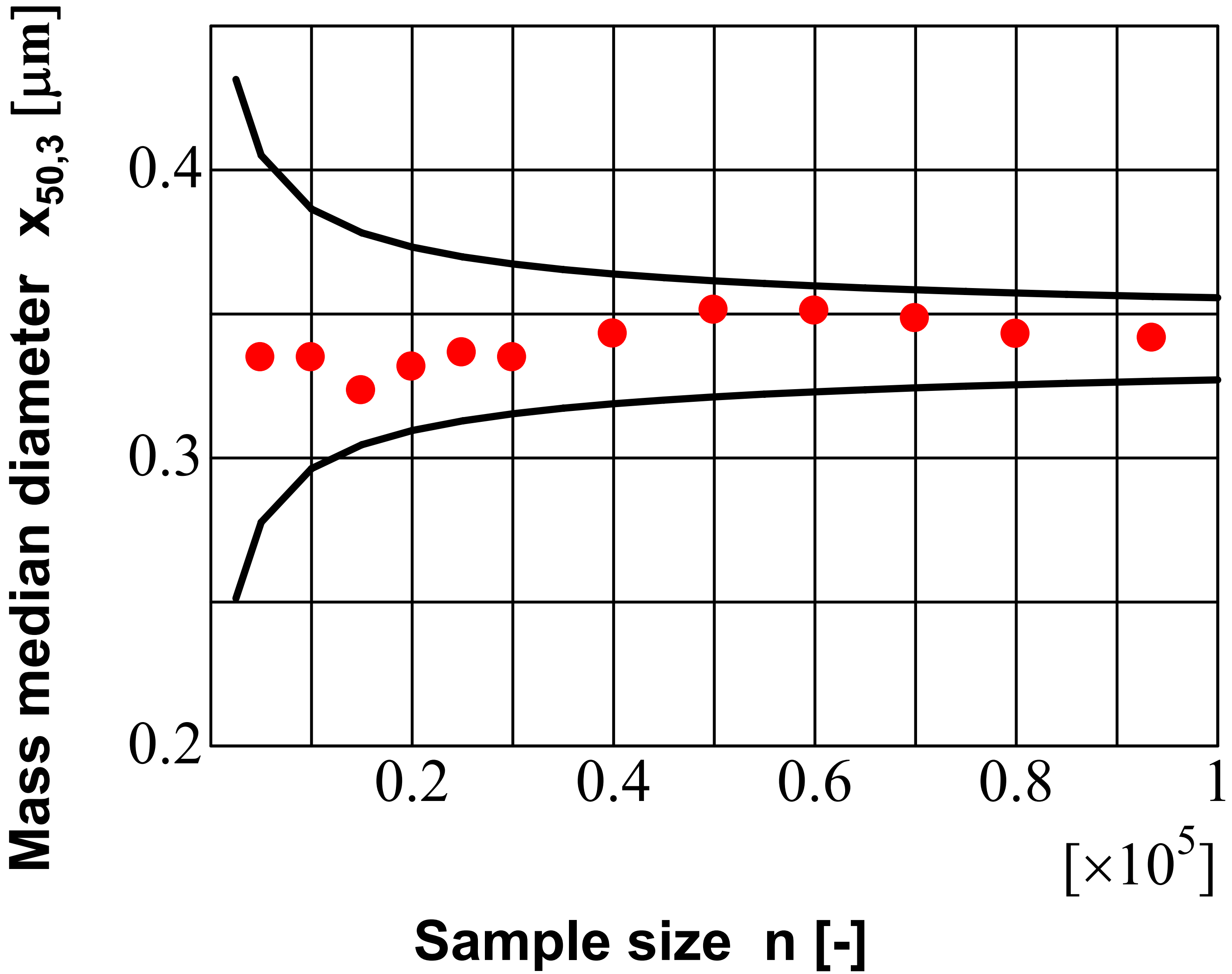

Fig.5 Mass median diameter for different sample size

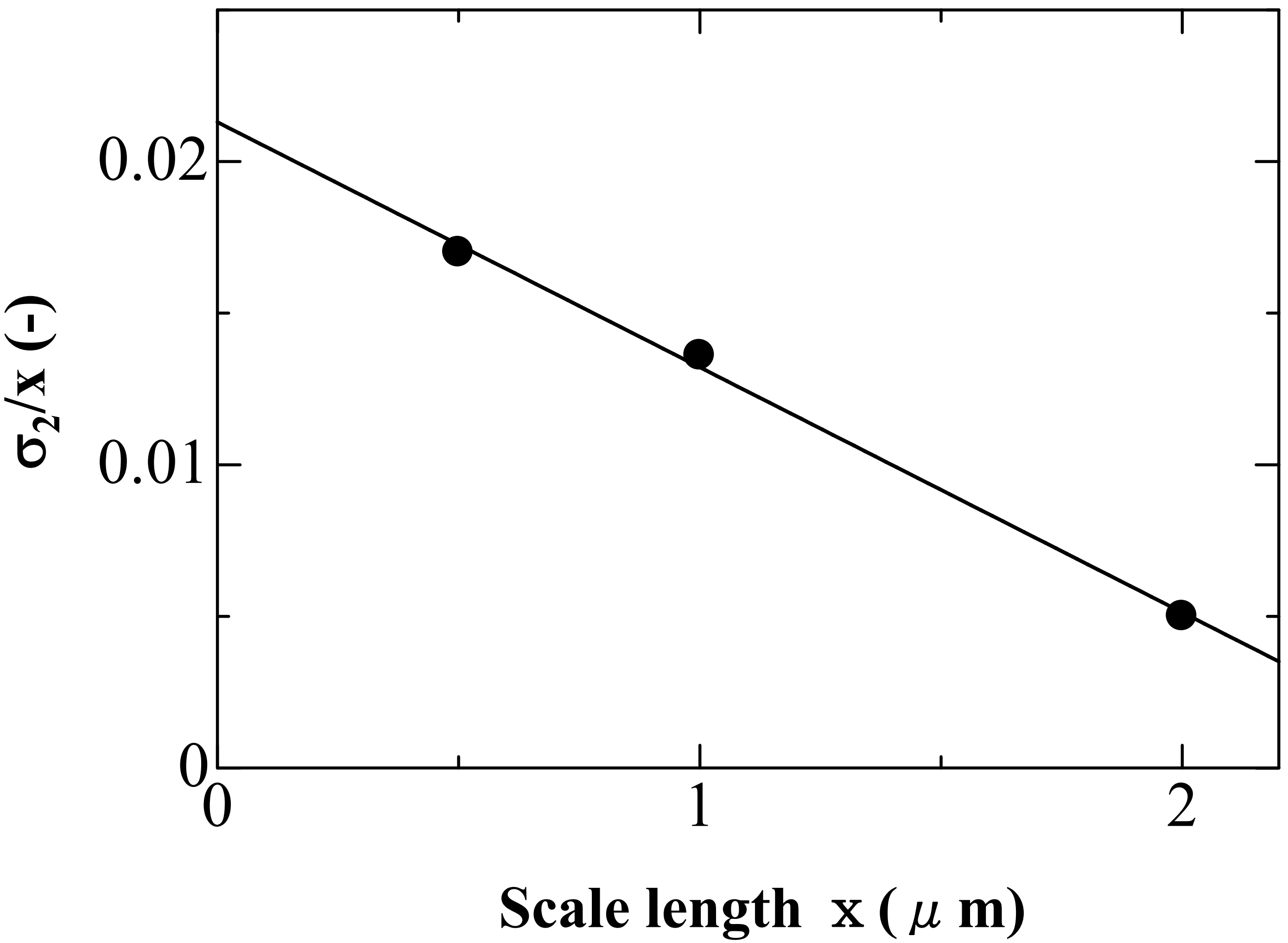

Fig.6 Uncertainty region of scale measurement

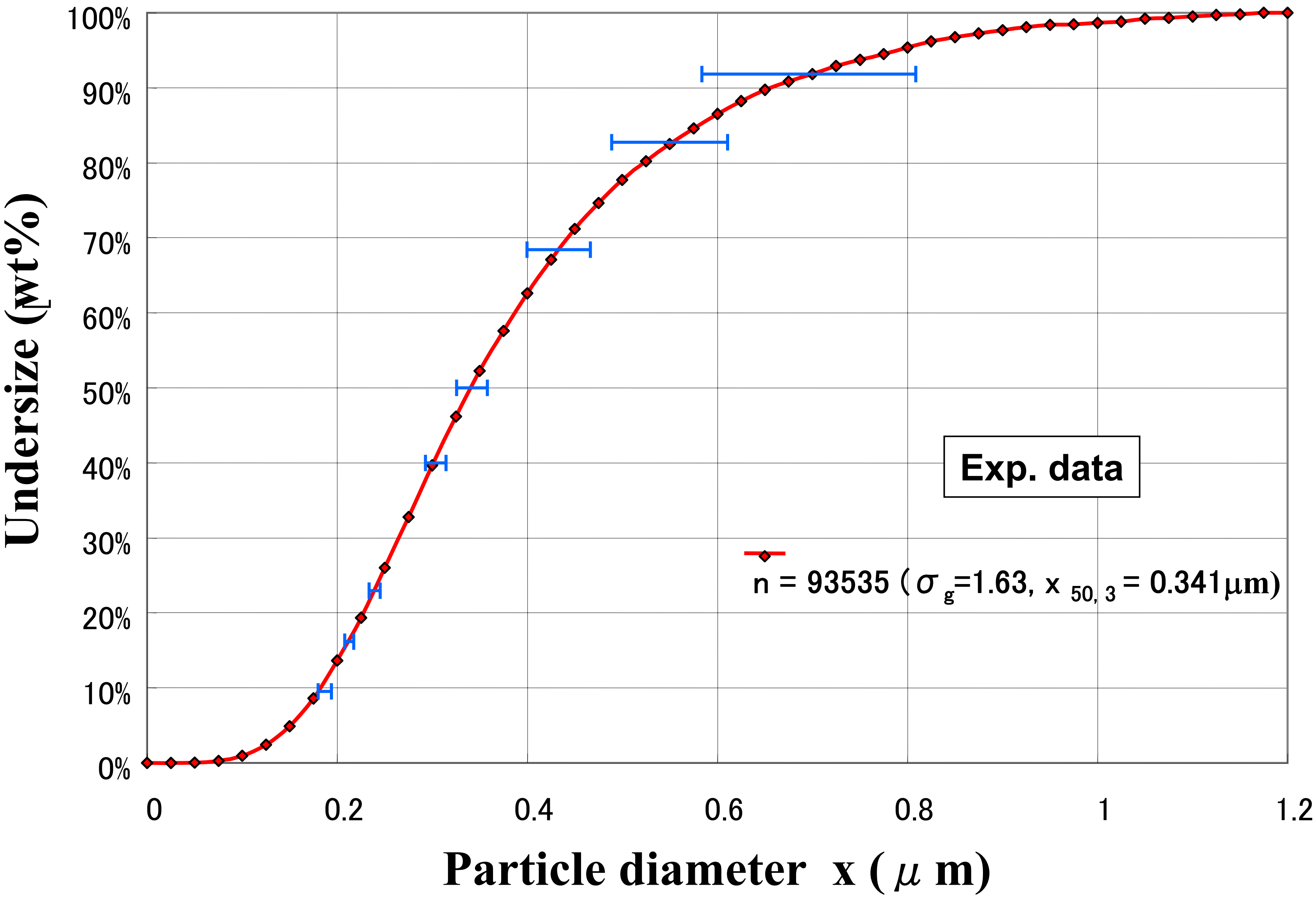

Fig.7 Particle size distribution with uncertainty region

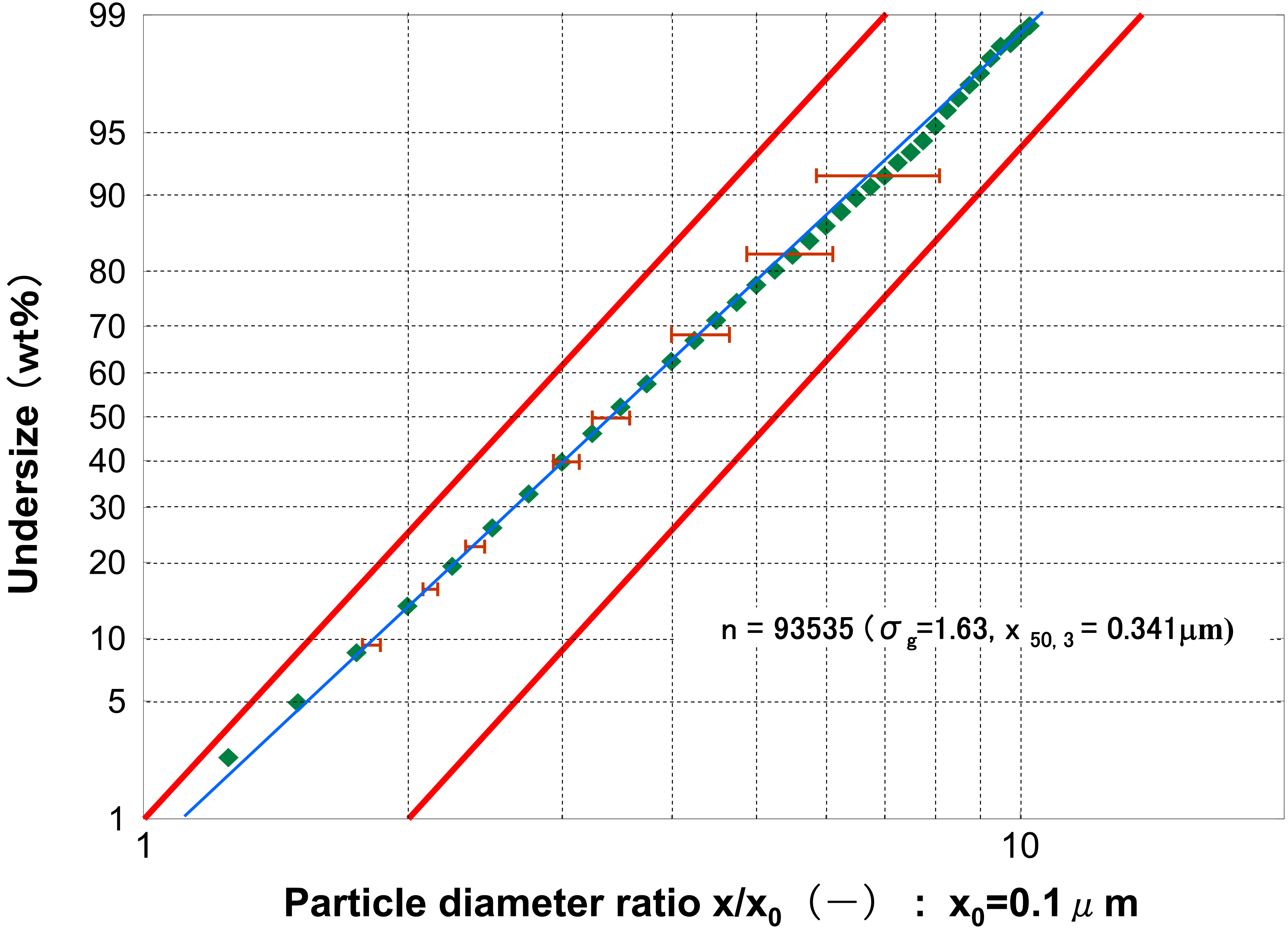

Fig.8 Partice size distribution indicated on log-normal sheet

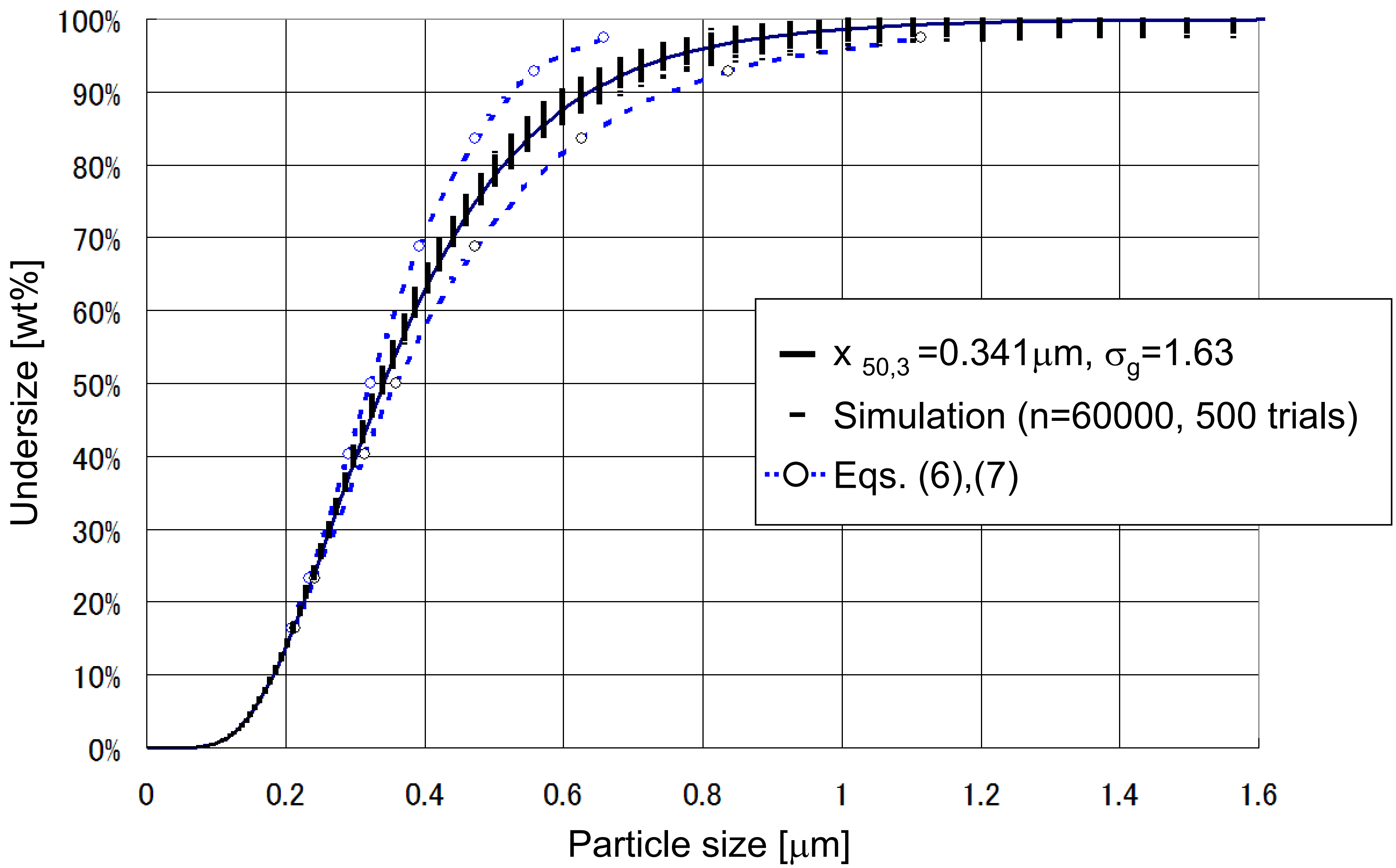

Fig.9 Simulation results of uncertainty region (500 trials)

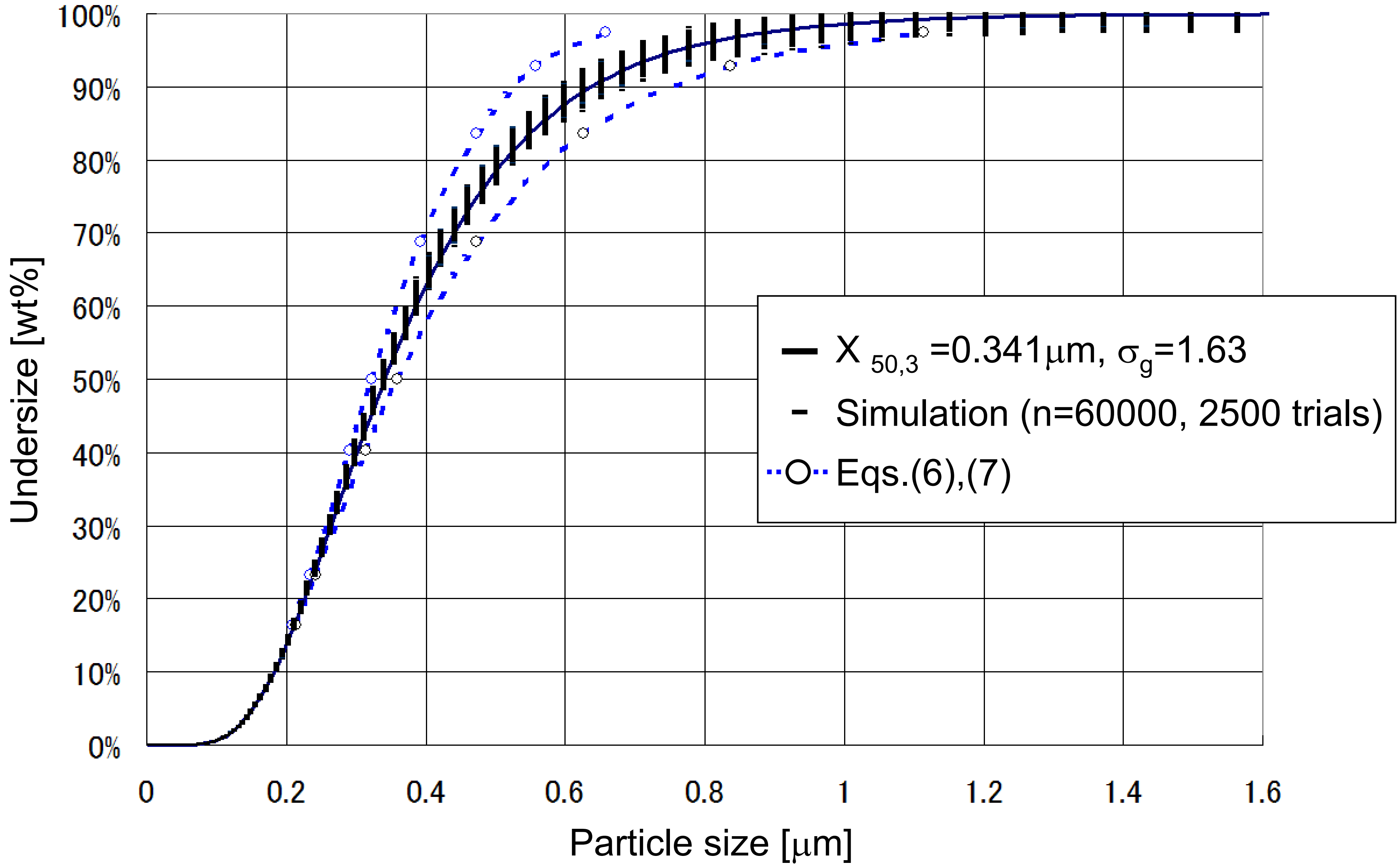

Fig.10 Simulation results of uncertainty region (2500 trials)

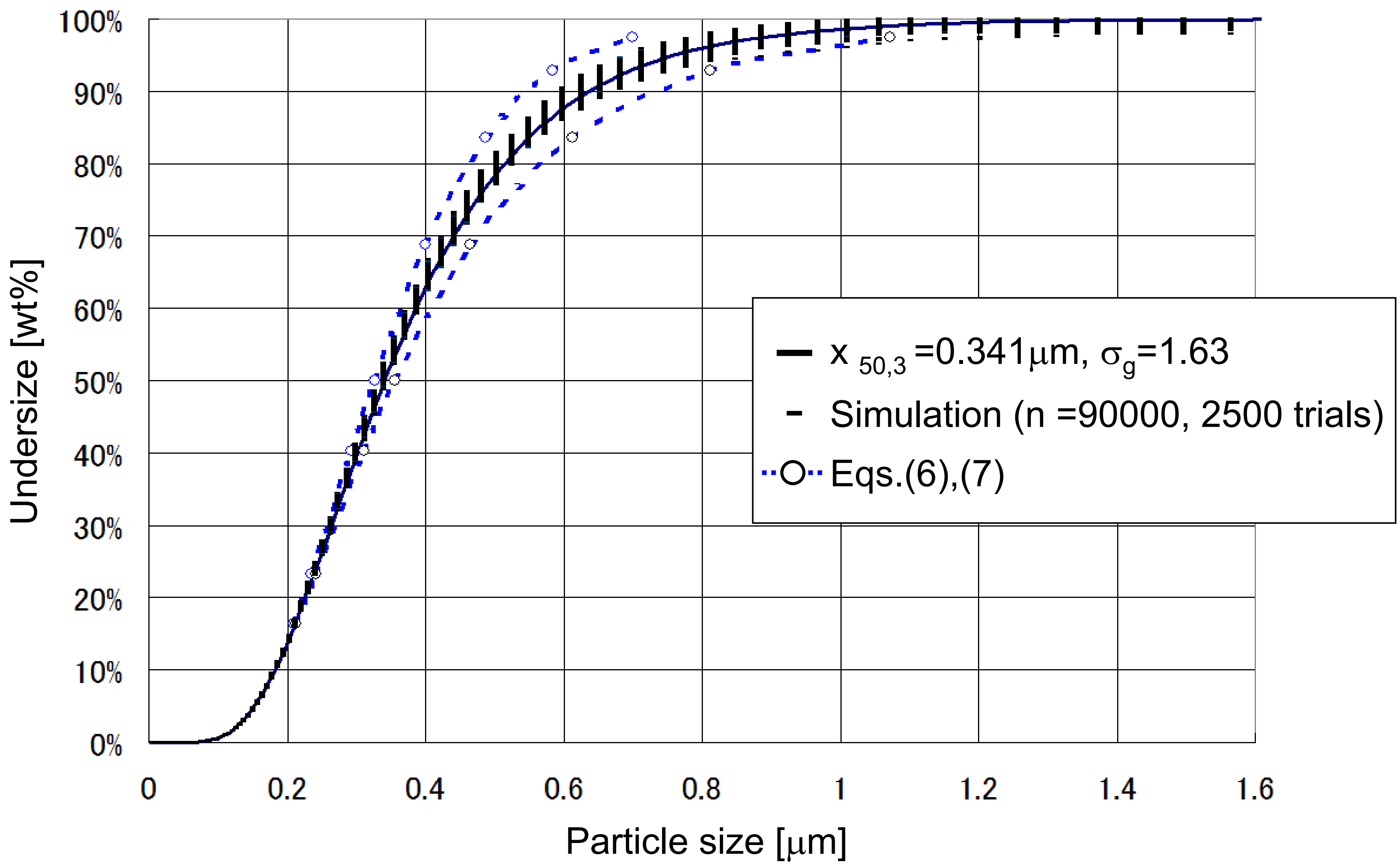

Fig.11 Simulation results of uncertainty region (n=90000)

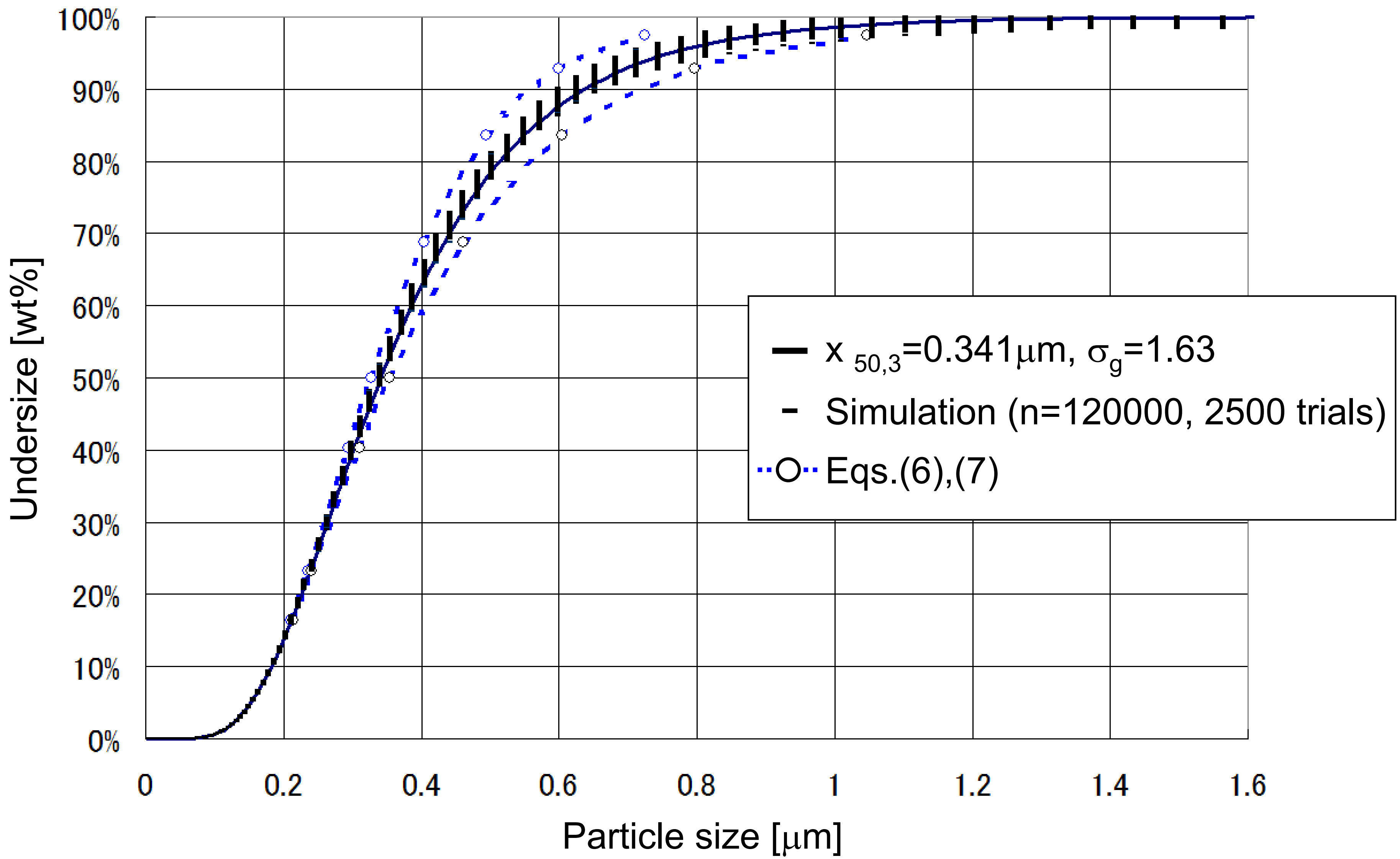

Fig.12 Simulation results of uncertainty region (n=120000)

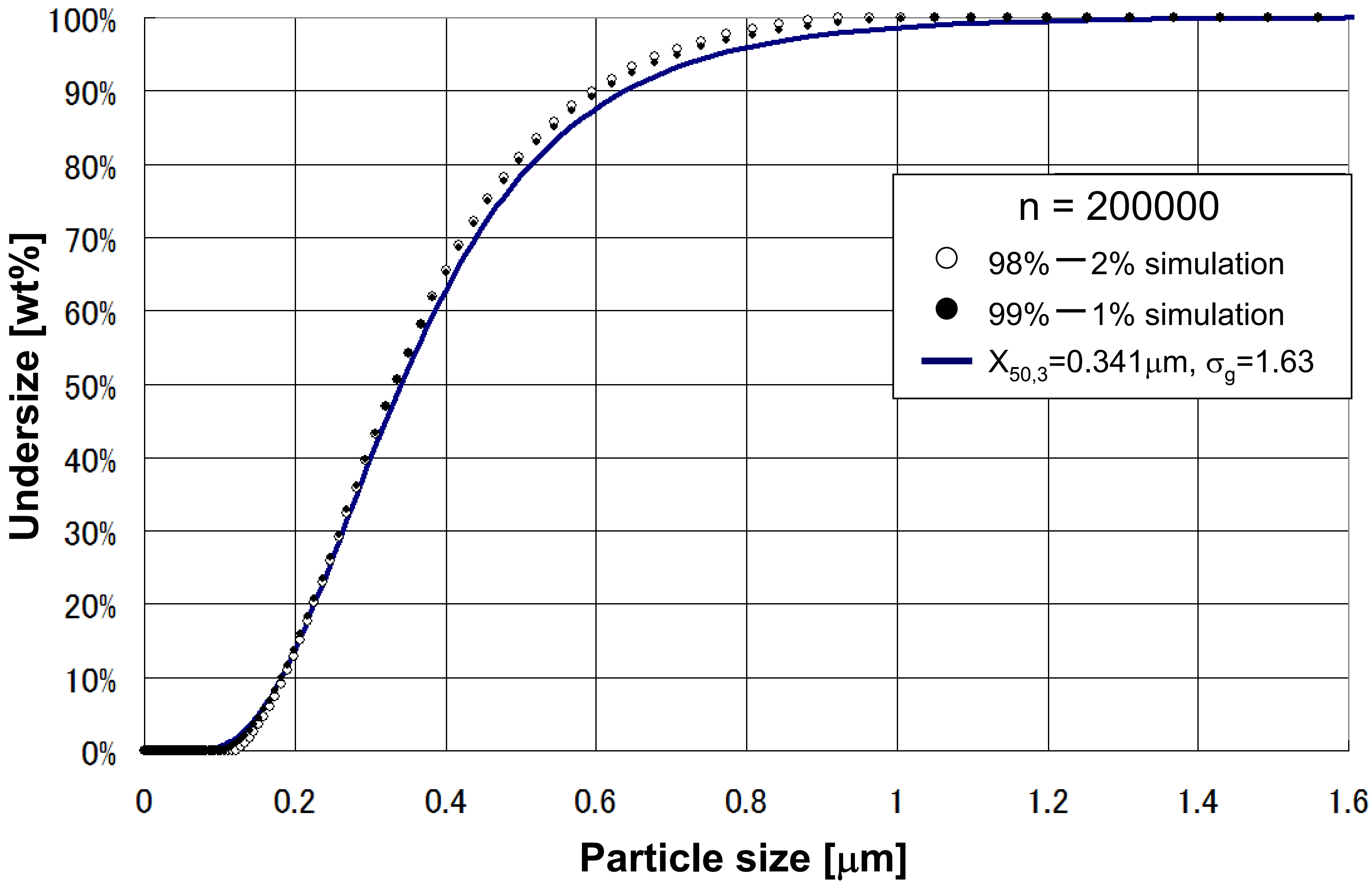

Fig.13 Simulation results of size distribution by selecting upper and lower size range (n=200000)

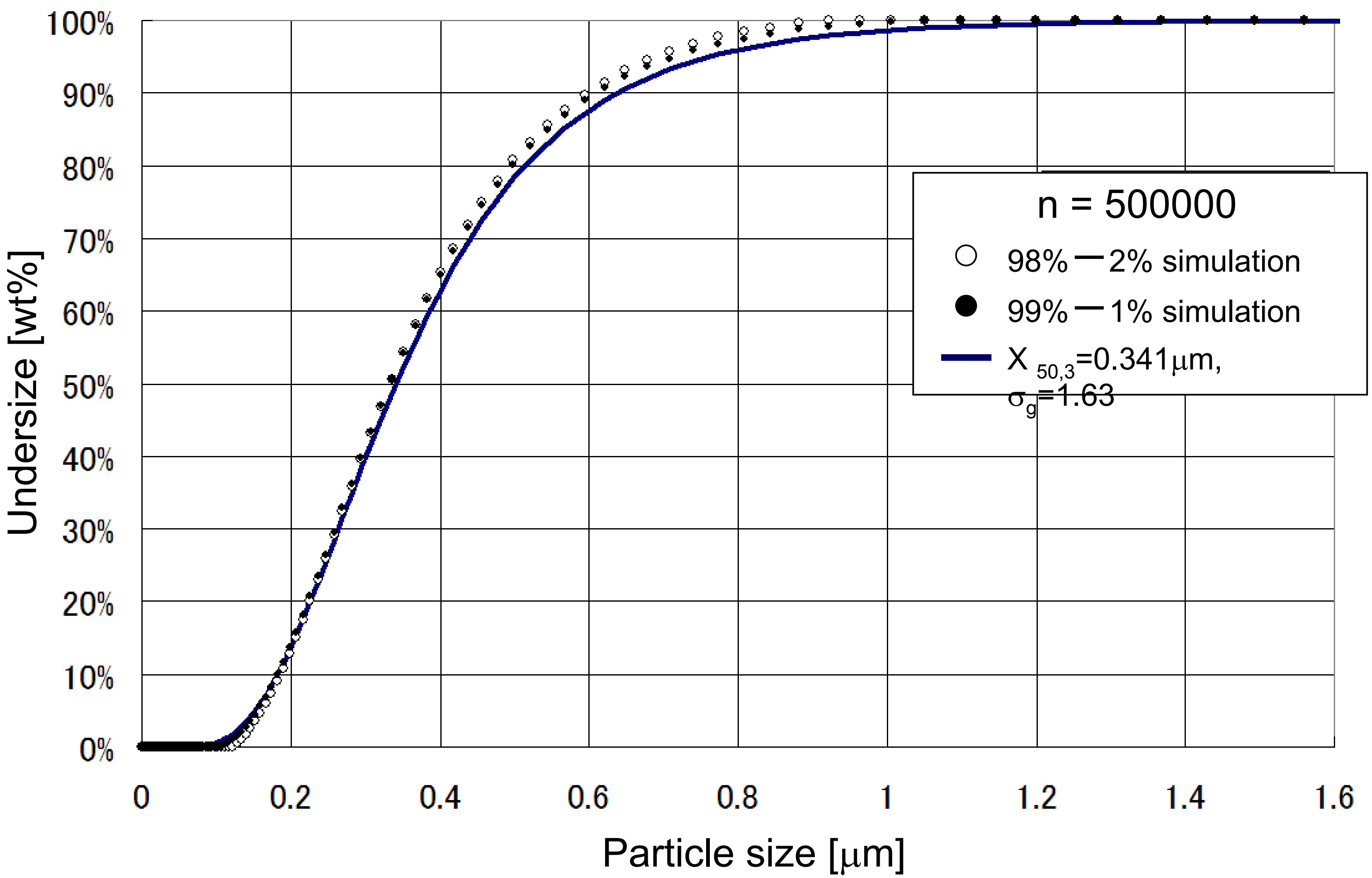

Fig.14 Simulation results of size distribution by selecting upper and lower size range (n=500000)