A STUDY ON THE REPRODUCIBILITY OF PARTICLE SIZE ANALYSIS USING LASER DIFFRACTION

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Abstract : Purpose of this study is to diminish the error of measurement and to increase measurement reproducibility in the process measuring particle size. Thus we suggested various analysis method, sampling, and statistical analysis error according to measuring frequency. This measuring technique using laser diffraction spectrometer has many advantages that simple operation gives easy measurement, measurement reproducibility was high, and measurement accuracy was effective because analysis speed was fast. Analysis reproducibility could be confirmed by comparing with other method and apparatus. For more precise measurement result, measurement errors by variety of particle size, dispersion, flow rate, an concentration variety of sample was indicated, and measuring time, focal plane, injection pressure drop, sampling method and dispersion effect were analyzed as measurement error according to apparatus system change.

Key Words : laser diffraction spectrometer, reproducibility, analysis method, sampling method

INTRODUCTION

Over the past few years, laser diffraction has become a very important method of particle size analysis in the field of environmental engineering. Typical features include the measuring range, the simplicity of operation and the speed with which analyses can be carried out. Optical particle counters which the particles pass successively into a measuring cell and emit a scattered light pulse effecting a change in transmission to an extent depending on their size have long been standard equipment in particle measurement. The laser diffraction spectrometer is simple to operate, measurement and evaluations are virtually completely automatic, and the time required is only a few minutes. Compared with,

for example, gravity sedimentation in the same size range between 10 and 100 μm, this implies very substantial rationalization and cost reduction. In contrast to many other methods, the laser diffraction spectrometer does require a calibration, special measuring liquids or an extremely low solids concentration.

BASIC PRINCIPLE

As an analyzing apparatus for measuring particle size, laser diffraction spectrometer(Helos, Sypatec, GmbH) is used, and this apparatus has been produced by applying Fraunhofer theory.[1] Wavelength of He-Ne laser in analysis apparatus is 632.8 mm, lens focal plane was 100~500 mm, and analysis method was regulated with wet and dry type.

The term scaling is used here to describe particular formulations or configurations of the scat-

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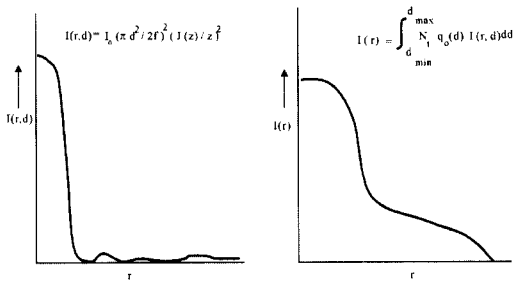Tel: +82-51-999-5273, Fax: +82-51-999-5652

Figure 1. Intensity distribution of Fraunhofer diffraction by particle distribution.

tering angles and size calsses, and a method for optimally scaling the systems is presented. Optimality is determined using several meassures of the stability of the resulting system of linear equation. The results provide design rules for specifying an optimal photodetector configuration of Fraunhofer diffraction particle sizing instrument.

In the Figure 1, if the particle is spherical, number distributing of particle in the cell express the scattered intensity distribution. I(r,d) is indicated intensity distribution of spherical diameter by Airy

$$I(r, d) = I_o \ (\pi d^2/2 \cdot f)^2 \ (J(z)/z)^2 \qquad (1)$$

In this, z is the particle size parameter $\pi rd/\lambda f$ and r is distance between lens and f is focal plane, d is particle diameter, λ is wave length, J is the Bessel function of first kind and first order, I_o is the on-axis(θ =0) scattered intensity and the dimensions of the intensity.

The scattered intensity producing according to spherical particle distribution number (N_t) could be presented by the sum of scattered intensity distributing by change of pattern that diffracting after

$$I_t = \sum_{i=1}^{Nt} I(r, d_i) \qquad (2)$$

According to the particle distribution number in the measuring cell, scattered intensity distribution I(r) is determined by pattern wide(s) that light is incidenced from the center of lens

to detector when particle is diffracted by laser intensity(I_o) incidenced according to change of particle diameter(d), focal plane(f), wave length (λ), laser incidenced in the measuring cell. In the laser diffraction spectrometer laser intensity(I_r), function deciding particle distribution (q_o(d)), is following

$$I(r) = \int_{d_{min}}^{d_{max}} N_t \ q_o(d) I(r, d) \, dd \qquad (3)$$

The particle size is shown in scattered intensity distribution chart by variable laser diffraction pattern incidence according to particle number distribution existing in cell.

Under those condition the intensity, I(θ), scattered at some angle, θ , in the far-fild is given by :

$$I(\theta) = I(0)(\frac{2 J_1(\alpha\theta)}{\alpha\theta}) \qquad (4)$$

where I(0) is the on-axis(θ =0) scattered intensity and the dimensions of the intensity, I, in Eq. (4) are power per unit soild angle. A distribution of particles, decribed by a probability density such that n(α)d α is the number of particle between α and α +d α , would scatter as :

$$I(\theta) = \frac{I_{inc} \ \lambda^2}{16 \ \pi^2} \int_0^\infty \alpha^4 (\frac{2 J_1(\alpha\theta)}{\alpha\theta}) n(\alpha) d\alpha \qquad (5)$$

where the on-axis scattered intensity, I(0), has units w/sr and the incident irradiance, I_{inc}, is in w/m^2.

The particle sizing problem requires that Eq. (3) be inverted, i.e. to provide information on the unknown particle size distribution, n, using measurements of scattered light which can be related to i(θ). The function given by Eq. (5) is known as the characteristic Airy diffraction pattern, which consists of a series of bright and dark concentric rings surrounding a bright center, with $\alpha\theta$=3.83. Now the number distribution, n(α), is not necessarily the function

of interest; rather it may be some moment such as the area or volume distribution function that is desired. Eq. (5) might improve the overall performance of the inversion. In fact, we propose to formulate Eq. (6) in the form:

$$i(\theta)\ \theta^a = C_1 \int_0^\infty \frac{J_1^2(\alpha\theta)}{\theta^{2-a}\ \alpha^{b-2}}\ n(\alpha)\ \alpha^b d\alpha \qquad (6)$$

where a and b are variable scaling parameters of inverse Fraunhofer problem.

A linear photodiode arry with equal area detector elements would have an output equal to i (θ) to within a constant, or $\alpha = 0$ in Eq. (6). A kernel function, k with scaling parameters is also defined :

$$k_{ab}(\alpha\theta) = \frac{J_1^2(\alpha\theta)}{\theta^{2-a}\ \alpha^{b-2}} \qquad (7)$$

so that the system Eq. (7) then becomes

$$i_a(\theta) = \int_0^\infty k_{ab}(\alpha\theta)\ n_b(\alpha)d\alpha \qquad (8)$$

which is known as a nonhomogeneous Fredholm integral equation of first kind as introduced by the Swedish mathematician Fredholm about 1900. Thus the particle's diameter can be calculated using integral equation suggested by Fredholmsch.[2] These can be divided into: integral transforms, i.e. analytical inversion of Eq. (8) by Hirleman[3]; reduction to a discrete linear system by numerical quadrature after Twomey and Rust and Burris[4,5]; and methods using functional analysis involving expansion of both the measured and unknown functions in terms of eigenfunctions after Bertero and Pike[6], singular functions after Bertero et al.[7], or fourier series after Lanczos.[8]

In order to assesse the accuracy of the particle size distribution obtained using this procedure, it is necessary to determine the degree of dispersion achieved. A Parameter, similar to one suggested by Leschonski,[9,10] has been defined which consists of the ration between two moments of the size distribution.

$$q_t(d)\frac{d^{t-r}\ q_r(d)}{M_{t-r,r}} \qquad (9)$$

From Eq. (3) and (9), the laser intensity distribution of spheres is given by

$$I(r) = N_t\ M_{-r,r}^{-1} \int_{d_{min}}^{d_{max}} q_r(d)\ d^{-r} I(r,d)dd \qquad (10)$$

It is following to convert particle distribution obtained from Eq. (9) into weight and volume distribution.[11]

$$q_3(d) = \frac{d^{-3}\ q_0(d)}{\int_{d_{min}}^{d_{max}} d^{-3}\ q_0(d)dd} \qquad (11)$$

In this, $q_3(d)$ is particle weight and volume distribution, $q_0(d)$ is diameter of particle number distribution.

The degree of dispersion was described by the moment related to specific surface the particles, $M_{-1,3}$. It has been determined from both dry analysis, $M_{-1,3}$, and from an analysis performed on a completely dispersed suspension of the same sample in a liquid, $M_{-1,3}$. The degree of dispersion was then calculated from:

$$\beta_{-1,3}/\ M^*_{-3,1} \sim S_r. \qquad (12)$$

If dispersion in the dry state is complete, $\beta_{-1,3}$ attains the value of one, with values between nought and one indicating the presence of undispersed agglomerates. The degree of dispersion, indicated by $\beta_{-1,3}$ values, indicates the influence of particle velocity, which is dependent on particle size, on the result. This causes the size analyses to appear coarser than they really are,[12] which is probably caused by the large particles emerging from the expander at lower velocities than the small ones and so spending a disproportionately long time in the measuring zone. If, however, the measuring zone is moved further down the axis, then the expanding free jet will lose velocity and slow down the small

particles, due to drag, to a greater extent than the large ones which possess more inertia.

EXPERIMENTAL APPARATUS METHOD

The experimental method was utilized Fraunhofer diffraction theory. For a more detailed and exact description, reference may be made to the relevant specialist literature.[13~15] The intention here is merely to give a greatly simplified, but clear, picture of the measuring process. Figure 2 shows three spherical particles of equal size which are exposed to parallel monochromatic light incident from the left. The light which is diffracted by the particles through a very specific angle is also parallel and is therefore focussed by a lens onto a particular point in the focal plane. This light, together with that diffracted other angles, gives rotationally symmetrical diffraction pattern in the plane which should not to be confused with the image plane. The undiffracted parallel light is collected at the focal point of the lens and overlaps the diffraction pattern at this point. The position of individual particles and their state of motion have no effect on the diffraction pattern. Thus, the measurement can be carried out on a free beam of particles or on a flowing particle suspension and air, and it is even possible to introduce a holograph into the light beam.

In the method of particle measurement, on account of representing measurement error by measuring system, the apparatus was made for dry and wet type analysis.
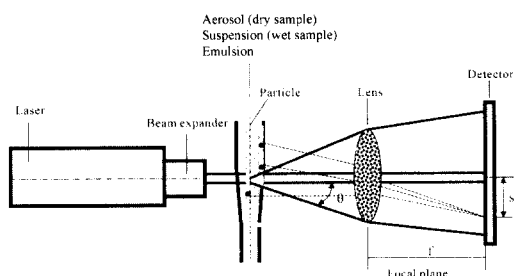

Figure 2. Schematic diagram of laser diffraction spectrometer.

In the method of wet type analysis, ultrasonic treatment was on the auto control in order to prevent flocculation during analysis. The method of dry type analysis consist of a feed hopper and vibrating chute, a rotary table with a U-shaped grove near its periphery, a scraper, a compacting roller and an ejector into whose inlet a rotating brush introduces the powder, followed finally by a cascade impactor which acts as a dispersing system. The particles leave the dispersion stage beam intercepts the solids laden free jet, with the volume of intersection forming the measuring zone. In the dry type, injection pressure was controled 1~5 bar. The detecter range of particle size in this apparatus can be 0.1~3000 μm. As the standard for particle analysis, Cement PZ 35, PZ 36, PZ 37 by Merke was used.

Analysis reproducibility could be confirmed by comparing with other method of measurement. In the wet type, compared depending on ultrasonic treatment and mixing time in measuring, the change of measuring concentration (Cv) and measurement error on solvent.

The measurement error appeared by variation of system in the apparatus was compared on measuring time and focal plane of lens. Also compared statistical measurement error on frequency in measuring and measuring method.

RESULT AND DISCUSSIONS

Effect of Measuring Method and Dispersing

The dispersants used can exert a very great effect, particularly if it is desired to study the agglomerate size distribution after very slight dispersion. Any comparison of the results obtained with various methods of measuring would be extremely problematic if the samples are affected by dispersion. Identical conditions for dispersion are seldom obtained, either by stirrers or ultrasonic devices or by the various dispersants. The stability of suspensions or effect of flocculants can be monitored by a laser diffraction spectrometer. Formerly, the only

economical means of determining the resistance of agglomerated particles to dispersion was continuous measurement of the specific photometric surface areas with increasing loading.[16)]

In order to show the variation of particle size on measuring method, the result of Figure 3 showed particle number distribution on measuring method in wet and dry in condition of standard PZ 35 that focal plane is 100 mm and measuring time is 25 sec.

In the wet type analysis, water used for dispersion solvent perform polarity in the sample dispersed measuring cell and then isopropanol was used for solvent to prevent change of size as particle .

In case of dry measurement, controled suppling injector pressure in 3 bar. The result on measuring method, if it compared with standards measuring results of Merke, though particle distribution in pine area decrease the loss of coarse particle area was presented. The reason of such an appearance is that bridge building between particle from small particle to among big particle in the measuring cell in case of using liquid for dispersionsolvent in measuring process.

As pressured air for suppling into measuring cell accelerate the activity of big particle, after changing laser diffraction pattern, as making big particle distribution decreased correlatively measuring error was produced on coarse particle.

In Figure 3, in case of using isopropanol for dispersion solvent, reproducibility was presented highly, the other side, in case of using H_2O, performing polarity measuring error was appeared highly due to effect of flocculation. In case of using H_2O for dispersion solvent, because these particles have intensive polarity and then as producing bridge building between particles, particles flocculation increases.

In Figure 4 shown limit error of 20 ± 6.5 μm comparing standard measuring result and reproducibility from Merke when H_2O is used according to solvent composition. Also in case of using isopropanol for solvent, measurement error is presented 20 ± 1.4 μm.
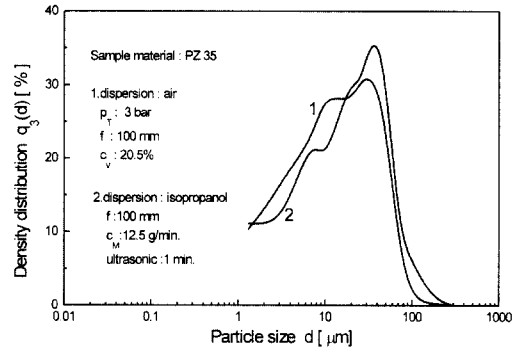

Figure 3. Variation of density distribution as a function of particle size measured by laser diffraction spectrometer.
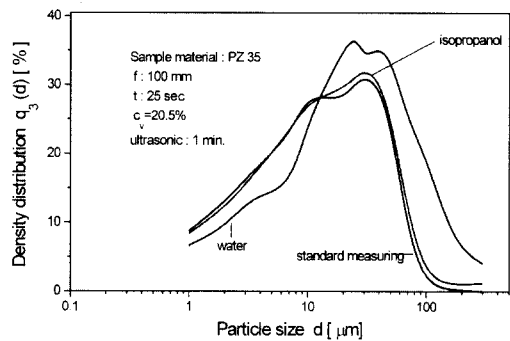

Figure 4. Variation of distribution as a function of particle size by the water and isopropanol at wet method in laser diffraction spectrometer.
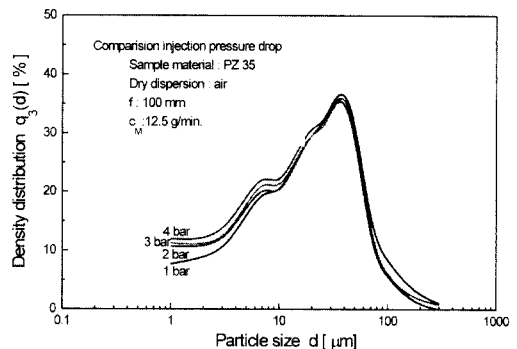

Figure 5. Variation of density distribution as a function of particle size by the injection pressure drop in laser diffraction spectrometer.

In Figure 5 was presented the result according to injection pressure of dry method that fine particle density distribution was decreased at 1 bar of injection pressure while large particle

density distribution was a bit increased and, at 4 bar, fine particle density distribution was increased while large particle density distribution was decreased. Therefore, particle distribution number was changed because the increase of pressure accelerates particles' mobility distributed in measuring cell and changes particle diffract pattern by laser beam.

The limit error shown in measurement result was 20 ± 2.5 μm at 1 bar, 20 ± 1.0 μm at 3 bar, and 20 ± 2.0 μm at 4 bar. Consequently, the highest reproducibility of measurement result was appeared at 3 bar.

Effect of Dispersing in Dry Method

This is confirmed by the behaviour of $\beta_{-1,3}$, shown in Figure 6, which reaches a maxima for measurements made at $30 \sim 40$ mm from the ejector exit with no impact stages, as well as with one and three impact stages. The greatest degree of dispersion is again seen to occur with three impact stages and the optimum distance of laser beam to ejector orifice of 40 mm, when $\beta_{-1,3}$ reaches a value of 0.96.

Figure 6 shows the effect discussed above on the particle size distributions while when the measuring zone is 40 mm away from the outlet the result shows good agreement with the reference analysis.

Figure 7 shows that the result varies according to variation of degree of dispersion with ejector driving P_T, 3 bar and nozzle spacing, s=5 mm in dry type method. It is observed that
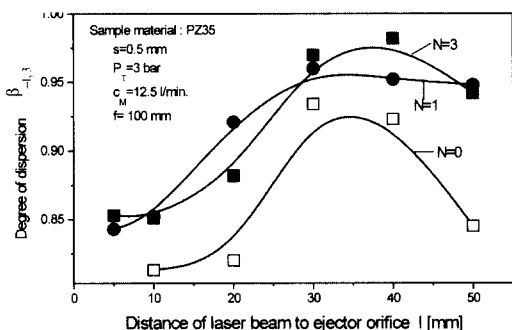

Figure 6. Maximum values of the degree of dispersion as a function of impact stages N, and position of measuring zone l.
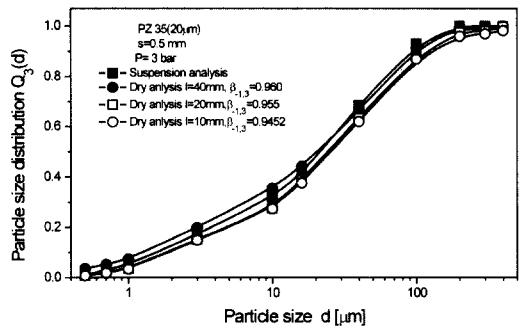

Figure 7. Particle size distribution by the ejector driving and nozzle spacing in dry type method.

the optimum position of measuring zone, $\ell = 40$ mm, as previously found, gives a degree of dispersion which increases monotonically with P_T until reaches value 0.96, at about $P_T = 3$ bar, after which it remains constant. Hence, mean particle was d50=19 ± 1 μm at 5 min of ultrasonic treatment in suspension, 20 ± 0.5 μm at $\ell = 40$ mm, 20 ± 0.5 μm at $\ell = 20$ mm, and 26.8 μm at $\ell = 10$ mm as effect of dispersion in dry methode. Consequently, the highest reproducibility of measurement result was appeared at $\ell = 40$ mm with ejector driving $P_T = 3$ bar and nozzle spacing, s = 5 mm in dry type method.

Effect of Dispersing Procedure in Wet Method

As was mentioned previously, the dispersion procedure exerts a substantial effect on the result of the measurements especially if agglomerates are present. Fine particles are to some extent, always are agglomerated.[17] The more intense dispersion, the better the deagglomeration and finer the resultant curve. An example of this is shown in Figure 8.

After ultrasonic treatment for Pre-treatment process is required for preventing flocculation, coarseness, and cohesion between particles in analysis process of particles. When using a solvent for dispersing particles which was measured as a liquid, pre-treatment process is complete mixing or method of ultrasonic treatment.[15]
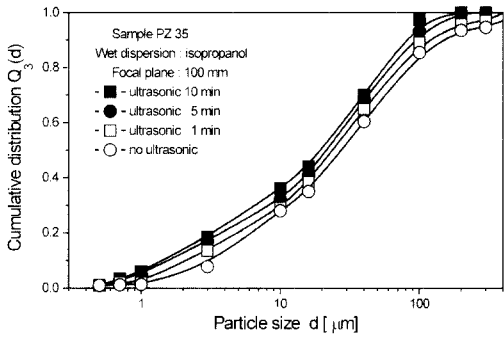
Figure 8. Cumulative distribution as a function of particles size by the ultrasonic preliminary treatment and mixing in laser diffraction spectrometer.

Figure 8 shows that the result varies according to treatment time of ultrasonic when using isopropanol as solvent in wet type method. Mean particle was d50=19.7 μm at 10 minutes of ultrasonic treatment, 23.2 μm at 1 min, and 26.8 μm at no ultrasonic treatment. Measuring limit error was slightly occurred because cohesion and flocculation effect between particles by Van der waals force and bridge building of particles when dispersion composition is liquid according to the increase of ultrasonic treatment for 10 minutes, dispersion at this intensity has no further effect. The distribution is very fine. Since measurement with a laser diffraction spectrometer takes only a few minutes and since the suspension is circulated continuously is not as critical as it is during a sedimentation.

Effect of the Sample Concentration

The volume concentration should be within a liquid to solids ratio of about C_v 4.2% to 28.5%. However, it is always advisable to check the effect of concentration. As shown in Figure 9, some products show substantial discrepancies within the stated range, although the upper or lower concentration limits are not exceeded. The finer the particles in the sample, the lower the concentration must to be. For a given product, and a given state of dispersion, the effect of concentration differs from one laser diffraction spectrometer to another.

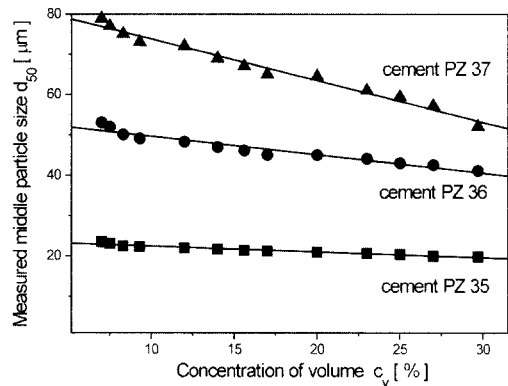When particle size is analyzed by using laser

Figure 9. Variation of mean particle size by the concentration C_v at the wet method in laser diffraction spectrometer.
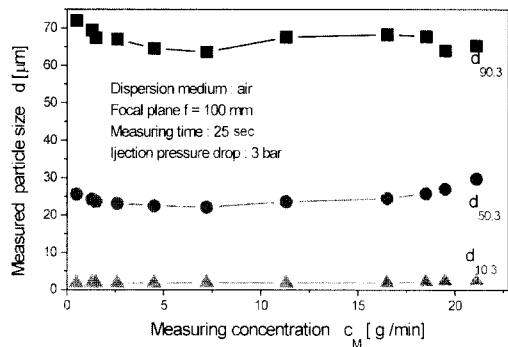

Figure 10. Variation of mean particle size by the concentration c_m(g/min) at dry method in laser diffraction spectrometer.

diffraction spectrometer, concentration in measurement cell has an effects on measuring result. When concentration of measurement cell is high, the measuring result is affected by increase of laser diffraction incidenced upon a particle. It's effective to measure concentration in measurement cell by keeping long distance between particles as possible, and by controlling width of laser beam not to be wide.

In the result of Figure 9, PZ 35 which has 20 μm mean particle size and PZ 36 which has 35 μm were analyzed by method of wet analysis using isopropanol as solvent. In method of wet analysis, measuring concentration C_v 20~30% shows the smallest measurement error.

As Figure 10 shows that the result of dry measurement, measurement concentration was supplied about 0.4~23 g/min. Comparing the

result of broken up concentration variation analysis, there are big error under 2 g/min and over 12.5 g/min. Particle size was decreased between 0.1~4.3 g/min and was increased slowly between 4.3~17.2 g/min.

The Result According to System Variation of Analysis Equipment

Measurement error by focal plane for angle control of laser light incidenced from analysis equipment was presumed following the result of dry method. Where f, laser lens focal plane, was controlled between 100~150 g/min. 'f' was designed to be able to measure f=20 mm when particles were distributed 0.1~35 μm, f=100 mm when 0.5~175 μm, f=200 mm when 1~350 μm, and f=500 mm when by 875 μm.

Following Figure 11, for measuring sample that has 20.5 μm mean particle size, there was no measuring loss for big particles when f was over 200 mm, but there was measurement error for small particles. In analysis result of particle size according to focal plane variation, there is the smallest measurement error when focal plane 'f' is 100 mm because mean particle size is 20.5 μm and particle distribution as 0.1~300 μm. During analyzing particles, measurement time changes the flow rate of particle by changing pump supplying rate in measurement cell. Thus measurement error is occurred through system change of analysis apparatus followed by flow rate change in measuring cell.

According to the result shown in Figure 12 statistically, measurement error was rarely occurred in 20~30 seconds.

Frequency number of measuring was represented important for the result of measurement to present reproducibility like particle distribution of result of standard particle analysis. Limit error range was appeared by using following statistical analysis model.

For analyzing error is occurred by frequency number of measuring limit error range of mean particle size analyzed continuously from three to forty times is shown using analysis model presenting following statistics. Where ts is mea-
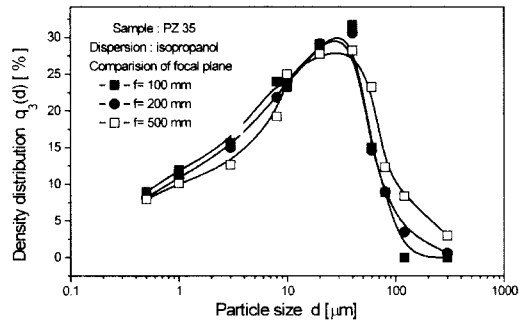

Figure 11. Cumulative distribution as a function of particle size by the distance of focal plane f and measuring time in laser diffraction spectrometer.
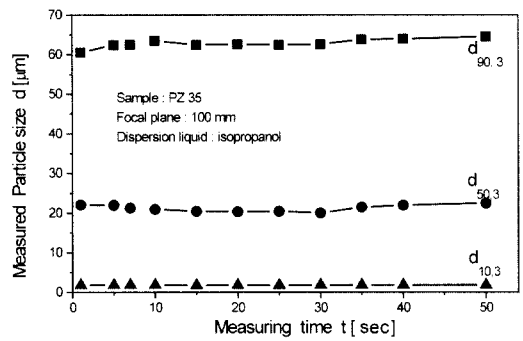

Figure 12. Variation of particle size by the measuring time at the wet method in laser diffraction spectrometer.
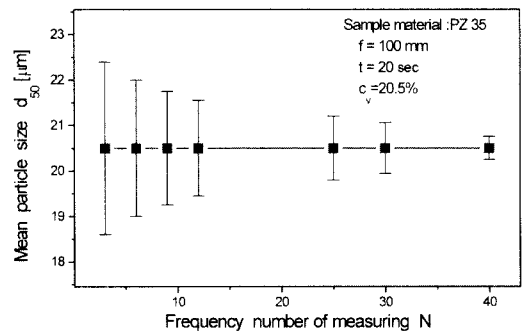

Figure 13. Variation of mean particle size by frequency number of measuring N.

suring factor and s is calculated by using value of s is deviation according to frequency number of measuring.

According to this model equation, limit range of measurement error calculated by using measurement result is shown in Figure 13. In this result, when the frequency number of measuring is 3

times, the range of limit error is 20.5 ± 1.9 μm, when 15 times, it's 20.5 ± 1.2 μm, and when 40 times it's 20.5 ± 0.25 μm. Thus if frequency number of measuring is increased, limit error range is decreased.

CONCLUSION

In this study, following results were brought out for raising reproducibility and reducing measurement error when analyzing particle size using laser diffraction spectrometer.

The experience thus gained and the knowledge acquired by direct exchange of experience with other test centres can be summarized as follows :

1. The reproducibility of a particular instrument was very good. The instrument was simple to operate. The measurements can be carried out very good. Agreement with other analytical methods was good, although in some cases there are discrepancies which cannot be explained.
2. In dry analysis method, measurement error was largely appeared when the size of particle distribution diameter was large, and in wet analysis method, the distribution diameter loss was large in fine particles due to condensation effect.
3. When analyzing particle size using water and isopropanol as dispersion solvent in wet analysis method, measurement error was 20 ± 1.4 μm using isopropanol for increasing condensation effect and 20 ± 6 μm using water.
4. In comparing measurement error and reproducibility according to pressure variation of instillation part in dry analysis method, it was the most effective when the pressure was 3 bar.
5. In considering ultrasonic of measurement pretreatment and the result of mixing pretreatment process, ultrasonic pretreatment times got longer, measurement error was small as condensation effect was reduced, and the measurement error of mixing pretreatment was small according to complete mixing

effect by 1 minute, but, over 1 minute, the error was larger for the increase of chemical and physical coherence in proportion as mixing time got longer.
6. Limit error according to concentration variation of sample supplied into measuring cell was the smallest in $20 \sim 30\%$ wet analysis method and it was also presented small in 5 g/min of measurement concentration in dry method.
7. Measurement error according to system change of analyzing equipment was the smallest when f=100 mm and was the most effective when measuring time was $20 \sim 30$ seconds in case of measuring sample which had 20.5 μm of mean particle size.
8. The investigation of a dispersing feeder has demonstrated that it is suitable for use in obtaining particle size distribution by means of diffraction pattern analysis, even with very fine powders, and that these analyses are comparable with wet analyses performed on liquid suspensions. In order to obtain reliable results it is necessary to condition and handle the power correctly in the feeding stage, and to deagglomerate it using both flow and impact forces in the dispersing stage.

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