Comparative Study of Particle Size Analyses Using Common Samples

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1. Introduction

The particle size is one of the most essential factors representing properties of powder or its system. Indeed, various instruments for particle size analysis based on various principles have been developed and used. The progresses are remarkable today in application of new principles, enhancement of performance, and rapid and simple measurement with introductions of laser, computer technology and the latest sensors. High-tech machines are coming onto the market one after the other, and more than 50 models are presently available; each of them gives reproductive data rapidly and easily only if you load a sample and press a button.

Traditional problems of particle size analysis are still unsolved in spite of these progresses in apparatuses. For example, if you compare the results of particle size measurements obtained by different principle or methods, they often do not give good agreement. This tendency seems to reside in the background of the diversification of the measuring principles and instrument models. One of the major factors is that the definition of a particle size obtained varies with each principle of measurement. The actual measured quantities are physical or geometrical quantities depending on the size of a particle; they are e.g., areas, volumes, sedimentation velocities, or the intensity distributions of scattered light. Based on these measurements, the particle size is always represented by a diameter, having dimension of length, of a spherical particle which gives the same observed quantity. This may be a natural reason of incoincidence in measured particle sizes except for spherical particles. Furthermore, the users face to a problem that the incoindences are observed in not only the results based on different principles, but also in the results measured by different models based on the same principle, or measured by different machines of the same model. It is hence important to compare various models mutually and to investigate the causes of the differences in the measured results.

The Society of Powder Technology, Japan, has been repeatedly tackling this problem. As early as 1961, the first "Particle Size Analysis Working Group" was organized, and joint measurements with various instruments using common samples were performed. Later, commercial models had been diversified by applying new principles and introducing new sensors and computers. In 1983, the second "Particle Size Analysis Working Group" was organized and joint measurement was projected. A comparative study on the various principles and instruments was performed comprehensively using seven common samples, and had given a great achievement. These common samples were, except for one kind, particles in the micron order or larger size, and the measurement of the particles in the sub-micron region was regarded little. The rapid progress in the material sciences and engineerings requires today the strict particle size analysis in the region of sub-micron, and many corresponding models have been developed.

The "Sub-Micron Particle Size Analysis Working Group" was organized as the third working group, and the principles and instruments have been studied in detail for more than four years since 1989. Following the tradition, the group's main activities were the joint measurements using common samples (six types). Based on these measurements, the agreements between the results given by different models were studied including theoretical discussions on the principles. The summary of the activities of the past four years and part of the achievements are reported here. The details are compiled and published in a book "Particle Size Analysis and Technology" (ed. The Society of Powder Technology, Japan, published by Nikkan Kogyo Shinbunsha; 1994). It should be read if interested.

2. Organization, activities, tested models

The working group was finally made up of 64 members from 22 universities and public research institutes, 15 user companies, and 14 makers and dealers.
The working group was organized into three classes as managing committee, small working groups and general meeting. The specific joint measurements were carried out by the small working groups with each principle. All members were, therefore, divided into ten small working groups shown in Table 1 (duplicate participation accepted). To classify the principle and method of measurement, various criteria would be available, and ten groups as shown in Table 1 were decided for the sake of convenience based on a certain viewpoint.

Each SMALL WORKING GROUP was chaired by the small group manager, and commercial models using the same principle were comparatively studied. Specifically, six common samples were jointly measured using the engaged models listed in Table 1. On the basis of the results, the theoretical and mechanical problems of the method and agreement among models were closely investigated. Each small group included makers or dealers engaged in the development or sale of the test model, and the features, problems, and handling cautions of the instrument from the aspect of both hardware and software were explained in discussions. They also participated in the joint measurement, and submitted their recommending optimum record. Their data and the other users' data were also compared. Based on these joint measurements, problems and noticed points in the measurement were studied for each model.

The MANAGING COMMITTEE consisted of the small working group managers and the persons in charge of study on sample preparation. The committee selected the common samples, measured and circulated the basic properties of the particles, and studied the sample preparation method. Discussions on comparison of different measuring principles were mainly performed here based on the data reported by the small groups.

At the GENERAL MEETING, specific reports by the small working groups and a comprehensive report by the managing committee were made, and the further specified study was carried out on the basis of their results. These studies disclosed some problems, and gave some solving method to be achieved theoretically or technically. These discussions were fed back into subsequent joint measurements.

3. Properties of common samples and sample preparation condition

3.1 Properties of common sample

Six kinds of powder were used as the common

| Table 1 Classification into the small working groups and tested models |
|---------------------------------------------------------------|
| Measuring principle | Small group manager | Tested models |
|---------------------|---------------------|---------------|
| Centrifugal sedimentation light extinction method | K. Suzuki (National Industrial Research Institute, Nagoya) | CAPA700 (Horiba) |
| | | SA-CP4L, SA-CP3 (L), SA-CP2 (Shimadzu) |
| | | SKA5000, MPS-Z (Seishin enterprise) |
| | | BI-DCP (Brookhaven) |
| Sedimentation X-ray absorption method | S. Edno (National Institute for Resources and Environment) | SediGraph 5100, SediGraph 5000D (Micromeritics) |
| | | BI-XDC (Brookhaven) |
| Laser diffraction and scattering method | H. Takano (Doshisha Univ.) | HELOS (Sympatec) |
| | | HR-850 (B) (Alcatel) |
| | | LA-500, LA-700 (Horiba) |
| | | LX20 (Coulter) |
| | | MasterSizer (Malvern) |
| | | MICROTRAC MKII SRA, SPA, FRA, (Reeds & Northrup) |
| | | SALD-1100, SALD-2000 (Shimadzu) |
| | | SK-PRO 7000S, LMS-24 (Seishin enterprise) |
| Optical blockage method | F. Ikazaki (National Institute of Materials and Chemical Research) | CIS-1 (Galai) |
| Electrical sensing zone method | H. Yamamoto (Soka Univ.) | Multisizer (Coulter) |
| Photon correlation method | M. Nakayama (Kokushikan Univ.) | AUTOSIZER (Malvern) |
| Chromatography | Y. Mori (Doshisha Univ.) | Unavailable in the market, house-made |
| Gas phase method | C. Kanaoka (Kanazawa Univ.) | DMA, Cascade impacter |
| Centrifugal sedimentation weight method | T. Yokoyama (Hosokawa micron Co.) | Differential pressure method |
| | | Unbalance method |
| Image analysis method | S. Endo (National Institute for Resources and Environment) | IP-3000 (Asahi Chemical Industry) |
| | | LuzexF |
| | | LA555 (Pierce) |

Note: Present positions of small group managers are shown
samples: they are abrasives WA#10000 and WA#8000, iron oxide (Fe₂O₃: α-hematite), and three types of monodispersed spherical silica particles with mean particle size of about 0.5, 0.9, and 1.4 μm. Table 2 shows measured values of particle density, refraction index, and ζ-potential of the samples. The measuring conditions for each property are also shown in the table. In the joint measurements, these properties were used as common conditions. Properties considered as suitable for a certain model (e.g., refraction index) were also determined for each model if necessary, and the measurement using such the values was executed again.

3.2 Sample preparation conditions

The sample preparation methods and their conditions were given the most regard in the joint measurement of the common samples. Of course, there is an adequate method of preparing samples for each principle and apparatus. Here, however, the following common conditions of the minimum limits were set to study the agreements between principles and between models. The small working groups took measurements in both specified common conditions and optimum conditions for each principle and instrument.

i) WA#10000, WA#8000, and iron oxide

dispersion medium: 0.05 wt% aqueous solution of sodium hexametaphosphate

mother liquor: Not particularly specified. Sample prepared as an appropriate particle concentration for each instrument from the beginning.

dispersion condition: Dispersion for 20 minutes in an ultrasonic bath. The power of ultrasonic waves is not specified.

ii) SP5H (0.5 μm spherical silica particles)

dispersion medium: 0.05 wt% aqueous solution of sodium pyrophosphate.

mother liquor: particle concentration of 0.1 wt% (5 wt% for X-ray method). It was diluted to optimum concentration for each instrument before measurement.

dispersion condition: Dispersion for 15 minutes in 300 W ultrasonic bath. Here, the sample container (beaker) was placed at the resonance point of the ultrasonic bath.

iii) SP9H, SP14H (0.9, 1.4 μm spherical silica particles)

dispersion medium: 0.025 wt% aqueous solution of sodium pyrophosphate.

mother liquor: particle concentration of 0.1 wt% (5 wt% for X-ray method). It was diluted to optimum concentration for each instrument before measurement.

dispersion condition: Dispersion for 15 minutes in 300 to 600 W ultrasonic bath. Here, the sample container (beaker) was placed at the resonance point of the ultrasonic bath.

The sample preparation condition i) was determined in the first days of this study, when the effects or the prepared amount of sample, hysteresis before measurement, and power of ultrasonic wave on the dispersion state of the sample were not known sufficiently, and therefore, the condition setting was somewhat ambiguous. Afterwards, as the working group activities were advanced and the informations were accumulated, the effects of the concentration of the mother liquor and the processing history and duration before measurements had been revealed. The search methods such as optimum dispersion operating point in the ultrasonic bath were also clarified, and hence, the conditions were set strictly for the measurements of silica particles. The relevant informations are also available in the book "Particle Size Analysis and Technology". 31

Table 2 Basic properties of the common samples

| Abrasive | Iron oxide | Spherical silica particles |
|----------|------------|---------------------------|
| WA#10000 | Fe₂O₃      | SP5H (0.5 μm)             |
|           |            | SP9H (0.9 μm)             |
|           |            | SP14H (1.4 μm)            |
| Particle density (x10⁵ kg/m³) | 3.74 | 5.01 | 2.25 |
| Refraction index (real number portion only) | 1.73 | 1.95 | 1.44 |
| ζ-potential | -67.9a) | -74.8a) | -89.9b) |

1) Mean of three measurements by auto-pycnometer 1320 (Micrometrics; air replacement method)
2) Measured at RIMS (Kyoto Fission Track Co.)
3) Measured with model 501 of PEN KEM (electrophoresis method)
a) In 0.05 wt.% aqueous solution of sodium hexametaphosphate
b) In 0.05 wt.% aqueous solution of sodium pyrophosphate
c) In 0.025 wt.% aqueous solution of sodium pyrophosphate
4. Results of measurements

There are numerous concepts regarding the method of comparison of the results, but, the results were summarized basically for the following principle in this report.

1) Results are summarized into one diagram for each sample and each principle of measurement, and the different models and instruments were comparatively studied.

2) The meaning of particle size obtained with each principle is basically classified into the follows:
   a) particle size by geometrical characteristics,
   b) particle size by dynamic characteristics, and
   c) particle size by optical characteristics.

Accordingly, the electrical sensing zone method, optical blockage method, image analysis method were divided into group (a), all of the sedimentation method including centrifugal light extinction method, X-ray absorption method, and centrifugal sedimentation weight method were divided into group (b), and Laser diffraction and scattering method and photon correlation method were also divided into group (c).

Because of limited pages in this paper, all data cannot be introduced. Please refer to the original paper\(^4\) for details.

4.1 WA #10000

Figure 1 summarizes the results of geometrical characteristic measurement methods, that is, the optical blockage method (dotted line), the electrical sensing zone method (solid line), and image analysis method (single dot chain line). In this case, the lower measurement limits of the optical blockage method and the electrical sensing zone method are 0.40 and 0.47 μm, respectively, and existences of the smaller particles are neglected; therefore, the results indicate rather larger particle size distributions, so these results should be regarded as only reference data. On the other hand, the image analysis method seems to miss the larger particles, because the number of particles measured was less than a thousand. The difference seen between the results of two models is suspected to be due to preparation method of sample images. In general, the scale shown on the sample image obtained with an electron microscope has an error of several percent, and it was found that there might be an error of nearly ten percent between sample images taken with different electron microscopes. Hereinafter, therefore, in the comparative study of image analysis, common sample images printed on the same scale from the negative taken with the same electron microscope were used.

Figure 2 compares two commercial models of centrifugal sedimentation light extinction method made by the same maker. The solid line shows the higher (later) model. The results of the higher model show four different measurement modes (three acceleration modes and one constant speed mode), and considerable differences are noted. The rightmost solid line, which indicates the result of the constant speed mode, shows the result of the larger particle size distribution compared to results of the other modes (acceleration). Here, it should be noticeable that the disturbance of the sample liquid occurs due to the convection or the like during the acceleration period until the rotating speed becomes constant. On the other hand, the results are also different depending on the models, but the model difference alone could not be blamed because the operators and places of measurement were different.

Figure 3 shows the results obtained with two models of X-ray absorption method. The solid line...
indicates the higher model, and here six results obtained by different operators (and different instruments) are shown. Although there is a slight difference at the fine particle size, the reproducibility is extremely excellent. A slight variation due to difference of model was also noted.

Figure 4 summarizes the results of dynamic characteristics (sedimentation). A difference arises depending on what is used to measure the successive change of the sedimentation amount of the particles. The solid line denotes the optimum data of three models (of three different makers) of centrifugal sedimentation light extinction method. The difference in the results would show the appearance of the difference in the correction method of the extinction coefficient proposed by each makers because this sample contains many sub-micron particles. A major weakpoint of the light extinction method is that the correction of the extinction coefficient for sub-micron order particle is necessary. This is because that the size of particle is similar to or lower than the wavelength of visible light (0.38 to 0.78 \( \mu m \)). By contrast, the X-ray absorption method (dotted line) does not require correction of the extinction coefficient as does the light extinction method. Hence, the difference between two dotted lines (different models) seems to be due to the difference in the instrument construction and data processing software. It is noticeable here that the weight method (differential pressure method, unbalance method) in the process of development coincides well with the X-ray absorption method.

Figure 5 shows the results of the laser diffraction and scattering method. Fourteen results obtained with seven models are shown. The dotted lines indicate the results of incomplete dispersion. Since

![](image1.png)

** Fig. 3 Results of WA #10000 by X-ray absorption method (2 models)

* Results of measurements in the optimum conditions of the instruments proposed by the supplier of the instrument, regardless of the common conditions.

** The power and irradiation time of the ultrasonic bath used by this operator were 300 W and 20 min, conforming to the common condition, however, this operator also reported similar data indicating incomplete dispersion with other principles and samples. This seems to be caused by the fact that the bath power was not in a rated state or the resonance point could not be found.

*** Afterwards, with the running of the common measurements, the instruments and softwares were improved, and the instrument constants came to be available for each model.
4.2 WA #8000

Figure 6 shows the results of the optical blockage method (solid line) and the electrical sensing zone method (dotted line). Distributions of this sample were within the measuring range of these instruments. The repeatability of the electrical sensing zone method is extremely excellent. Difference in the results of the optical blockage method was probably due to instrumental errors and difference in sample concentration.

Figure 7 shows the results of the centrifugal sedimentation light extinction method (dotted line) and X-ray absorption method. It could be considered that there was a difference in the strict sense; however, in comparison to the results of WA #10000, it is reasonable to regard that these results coincided with each other. This is due to absence of the sub-micron particles; accordingly, this sample gives no difference due to the correction of the extinction coefficient. The difference in maximum and minimum diameter seems to be owing to the instrument construction and operating conditions.

In Figure 8, the results of the centrifugal sedimentation weight method (dotted line) are overlapped on Figure 7. These good coincidences with the results of the light and X-ray method make a expectation of the practical use of this method.

Figure 9 shows the results of the laser diffraction and scattering method. The figure shows 26 results obtained with 7 models. Although not clear in the figure, the reproductivity is superior with the same model. There is, however, a difference at the fine particle size, and a slight difference is noted depending on the models. Besides, as compared with other principles of the measurement, all models provided larger values with a significant difference. The cause of this is unknown.

4.4 SP5H (monodispersed silica spherical particles of around 0.5 μm)

Figure 10 shows the results of the image analysis method (solid line, 3 models) and the electrical sensing zone method. With the electrical sensing zone method, the lower limit of measurement was 0.32 μm, therefore, this should be regarded as an only reference data. The result of the image analysis method shows
a very narrow distribution. A slight difference at the fine particle size is due to a difference in the image processing and conversion method into the diameter of the corresponding circle. Although the same sample images were used, the number of particles extracted to analysis was slightly different.

Figure 11 shows the results of the centrifugal sedimentation light extinction method (4 models, 6 results). The data indicated by the solid line and the closer (2 models) were corrected with the extinction coefficient, while other three results indicated by dotted line were not corrected; they caused some differences. The dotted line shows three results obtained with one model, and two lines from the right indicate the rotating speed of 3000 and 5000 rpm in its order. The lower rotating speed causes the greater centrifugal dilution effect (see chapters 4 and 5 of "Particle Size Analysis and Technology"3), and the results show as if non-existent large particles were present. The other dotted line shows the result after correction of the data at 5000 rpm with respect to the centrifugal dilution effect. The enhancement of the larger particles distribution has been successfully corrected. In the case of the sample having a wide distribution, it seems that the centrifugal dilution effect is less obvious. On the other hand, in the case of a narrow distribution as in this sample, the correction is necessary because it appears so significant that it cannot be ignored. The single dot chain line on the right side shows the result obtained with the model using a line start method (without correction of extinction coefficient). The line start (simultaneous sedimentation) method maintains the sample particles at a certain sedimentation liquid surface, and allows them to sediment centrifugally at time $t = 0$ simultaneously. Therefore, as far as the successive changes of particle concentration of the same measuring surface are observed, no correction on the centrifugal dilution effect is necessary, because the sedimentation distance is identical and, therefore, that effect is the same for all particles of any size. Accordingly, it coincided well with the result of the light extinction method when the correction for the centrifugal dilution effect (the leftmost dotted line) was introduced.

Figure 12 shows the results of the X-ray absorption method. The solid line shows the results of the same model (gravitational sedimentation), while the operator (instrument) was different. The long tail on the coarse particle side is due to poor dispersion. The dotted line represents the data of the model used for centrifugal sedimentation. From this point of time, the model using the centrifugal sedimentation comes to be available for the X-ray absorption method.

Figure 13 shows the results of the laser diffraction and scattering method (solid line: 5 models and 7 results) and photon correlation method (dotted line). There are considerable differences as from narrow to wide distributions depending on the models. In
general, if the refraction index is adjusted to the measured value or reported value, a considerable difference appears in the results depending on the models. This is because that the refraction index of the measured or reported value is not an optimum for each instrument, but each instrument has its own optimum value. The photon correlation method (dotted line) provides a narrow distribution and the mode diameter is close to 0.5 \( \mu \text{m} \). This fact suggests that the photon correlation method is very useful for monodispersed samples under sub-micron size. In the present study of the working group, the data of the photon correlation method could not be accumulated sufficiently, but this method is expected to be used widely for the measurement of sub-micron samples in the future, and it is necessary to investigate this method closely in the near future.

### 4.6 SP14H (monodispersed silica spherical particles of around 1.4 \( \mu \text{m} \))

Figure 14 shows the results of the image analysis method (solid line: 3 models, 3 results), the electrical sensing zone method (dotted line), and the optical blockage method (single dot chain line). Both the electrical sensing zone method and the optical blockage method cover the size distribution of the sample particles in their measuring range. The optical blockage method gave results with broad distribution in comparing to others. The electrical sensing zone method (dotted line) gave results coinciding with results of the image analysis method, but gave a tail in the coarse range. This is caused by the phenomenon that the particles do not pass through the center of the aperture (here, we called it "wall vicinity pass effect"). The electrical field strength near the wall is relatively larger than it at the center, a particle passing near the wall is observed as a somewhat larger particle (see chapter 11 of "Particle Size Analysis and Technology" for detail).

Figure 15 shows the results of the centrifugal sedimentation light extinction method (5 models, 8 results). Here again, the distribution of the larger particles was enhanced in the results of the model not corrected for the centrifugal sedimentation dilution effect. The dotted line represents the result of the line start method. It is observed as a narrow distribution very close to the results of the image analysis method shown in Figure 14.

Figure 16 shows the results of the X-ray absorption method (2 models, 5 results). The gravitational sedimentation method (solid line) gave a wide distribution. The results of the centrifugal sedimentation model (dotted line) indicated a narrow distribution, and they nearly coincided with the dotted line in the previous figure. These models were made by the same maker. In the case of that the same maker supplies models based on different principles, the results are often coincident, which should be taken into consideration.

Figure 17 compares the results of all sedimentation methods. The single dot chain line represents the results of weight methods. A considerable difference is noted depending on the measured physical quantity.

Figure 18 shows the results of the laser diffraction and scattering method (9 models, 12 results), and photon correlation method (dotted line: 1 model). The results of the laser diffraction and scattering method were considerably different as in the cases of other silica particle samples. The photon correlation method
gave results as the smaller particles. The upper measurement limit of the photon correlation method seems to be about 1 \( \mu \text{m} \).

5. Conclusions

Unfortunately, all data cannot be introduced within the limited number of pages of this paper. For details see the original paper. From the limited data disclosed here, it may be at least understood that agreement of the results is not sufficient for principles, models and instruments. The cause is not sufficiently discussed herein. The details should be discussed by the readers themselves who are well versed in the features of the principles and apparatuses of these measurements.

Anyway, the apparatuses will continue to progress, and the progress will perform more and more in the automation and simplification of the operation and of data processing. Accordingly, the skill of the operator will be less required, and factors causing the error will decrease drastically. As the results, the process will be automated from measurement to data processing, requiring no human help, and the intervention of human will decrease more and more. Ultimately, the instrument may present the data while man could not know how the process is performed. In order not to be ruled by the data, the user is asked to be wise and clever, and is requested to understand the principle and features of the instruments. We shall be pleased if the achievements of our working group studies are of any help to the readers for correct measurements and evaluations depending on the purpose, by making the best use of the features of individual instruments.

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Hideo Yamamoto was born in 1943 in Tokyo and graduated from the Department of Chemical Engineering, the University of Tokyo, in 1967. He received the Dr. Eng. degree from the University of Tokyo, in 1979. He joined the Department of Chemical Engineering, University of Tokyo in 1976, and in 1989 to become an Associate Professor at the Institute of Industrial Science, University of Tokyo. He was a Visiting Researcher at Delft University of Technology, in The Netherlands, from 1984 to 1986. He joined the Department of Bioengineering at Soka University, as a Professor in 1991. His field is particle technology and applied electrostatics. His current researches are particles separation from gases, fine powder dispersion in gas, particle size analysis, production and application of ultra fine particles, triboelectric charging of polymer particles, high temperature electrostatic precipitation, electrostatic formation of ceramic membrane, chemical reaction in surface corona plasma, and electrostatically handling of biomaterials.

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