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# Comparisons of particle size measurement method for colloidal silica

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**Several methods have been used to measure the particle size and distribution of colloidal silica. It is an important parameter governing the proper function of many industrial products, for example, organic-inorganic hybrid coatings, ceramic coatings, paints, and inks, etc. Particle size distribution of commercial colloidal silica of eight was measured by TEM (transmission electron microscopy) or DLS (dynamic light scattering). The accuracy of the particle distribution is decreased when the colloidal silica is a mixture of approximately 50 nm particles and 100 nm particles. The particles less than ~50 nm may not be detected by DLS analyzer in the case of mixture sample. In order to investigate the difference in particle size distribution among measurement methods, we have compared and discussed particle size results measured from DLS, TEM, and BET (Brunauer-Emmett-Teller) analysis. In the TEM observation, 16 TEM images from one grid were compared and found out that the particle size distribution may vary based on the positions from which the particles are observed either scattered or agglomerated. We suggest combination of DLS, TEM and BET method to obtain the particle size distribution reflecting the dispersion, which represents the surface properties and aggregation state.**

**Key words: Colloidal silica, TEM, Dynamic light scattering analysis, BET analysis, Particle size distribution.**

## Introduction

With the advent and development of nano technology, nano-sized particles have been applied in various fields such as electronic ceramic, semiconductor, ink, functional coatings for optic glass or film, fillers of cosmetic and CMP (chemical mechanical polishing) abrasive slurry or etc. The accuracy of particle size measurement is becoming increasingly important since this directly affects product performance. [1, 2] The measurement of particle size distribution is required in understanding the development of new materials, process conditions and environmental factors. For instance, particle size measurement is important for synthesis of nano-sized particle and performance of abrasive particles in the CMP process. [3]

The methods used for measuring particle size distribution are: electron microscopes, light scattering and disk centrifuge photosedimentometer (DCP). In cases of electron microscopes, we first take images of spread particles and make an overall analysis. Electron microscopes are highly accurate tool for measuring particle size because it directly observes the particles. However, electron microscopes observe only a small part of the sample, so accuracy could be low. In light scattering method, the particles are observed at a suspension state, whereas in electron microscopes observation method, the samples must be dried and coated in cases of silica with gold or platinum. By such processes the samples could lead to a contraction of particles which would result in a smaller particle in comparison with the light scattering method. In case of TEM, contrast between particles and background, image type (bright or dark image) and magnification etc. can cause the deviation of measurement result. These errors appear more frequently from 30 to 50% in cases of small particles within the range of 1 ~ 1.5 nm. [4]

The light scattering techniques are divided into two types; namely static laser light scattering (SLS) and dynamic laser light scattering (DLS) method. The particle size and distribution are analyzed through detecting the wave length signal change of scattered light. SLS is the measurement of the angular distribution of a time averaged scattering intensity. The scattering intensity of the sample is measured as a function of the scattering vector. Contrary to SLS, DLS relies on the statistical fluctuations of the scattered light due to the Brownian motion of the particles in the control volume. While the SLS method is appropriate for measuring submicron ~ 300 um sized particles, the DLS method is suitable for measuring 1 nm ~ 1 um sized particles.

The equipment used under the SLS and DLS method is appropriate when measuring mono dispersed samples and also device control is simple and easy However, in poly-dispersed samples, the results have shown that it is difficult to measure the exact size distribution. [5, 6]

Disk centrifuge photosedimentometer (DCP) is a technique based on the principle of particle movement induced by a centrifugal force. This method is difficult to analyze nano-sized particles accurately because

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**Table 1.** Properties of commercial colloidal silica investigated.

| Sample number | commercial name | Nominal size (nm) | pH | Stabilize ion | | Supplier |
|---|---|---|---|---|---|---|
| M-1 | SM-30 | 7 | 10 | Na | 0.56 | Aldrich |
| M-2 | HS-40 | 12 | 9.7 | Na | 0.41 | Aldrich |
| M-3 | CL | 12 | 4.5 | Cl | 0.5↓ | Aldrich |
| M-4 | ST-AK | 10-15 | 4 ~ 6 | Al | 1.5 ~ 2.7 | Nissan chemical |
| M-5 | ST-C | 10-20 | 8.5 ~ 9 | Na | 0.2↓ | Nissan chemical |
| M-6 | TMA | 22 | 4 ~ 7 | - | - | Aldrich |
| M-7 | ST-20L | 40-50 | 9.5 ~ 11 | Na | 0.3↓ | Nissan chemical |
| M-8 | ST-ZL | 70-100 | 9 ~ 10 | Na | 0.07↓ | Nissan chemical |

**Table 2.** Samples of bimodal colloidal silica sol. mixing ratio of M-7 and M-8; $D_{TEM}$ measured by TEM; $D_{DLS}$ measured by DLS.

| Sample number | Mixing ratio (M-7 : M-8) | $D_{TEM}$ (nm) | $D_{DLS}$ (nm) |
|---|---|---|---|
| B-1 | 2 : 8 | 129 | 131.1(± 5.7) |
| B-2 | 5 : 5 | 86 | 128.5(± 5.4) |
| B-3 | 8 : 2 | 68 | 109(± 3.1) |

these particles are affected by Brownian motion as well as centrifugal force. [6]

As mentioned above, the measurement result of colloid particle can vary depending on the equipment used. Thus, it is necessary to understand and analyze the morphology, distribution and size of particle using various equipments such as electron microscopes, DLS and DCP; rather than using only one tool in observing the size of the particle. If the colloidal silica particles are uniform and spherical, the BET, TEM and DLS methods shows similar results. In this study, we measured 8 kinds of commercial colloidal silica using DLS, TEM and BET and compared its mean particle size.

In DLS method, since the particle size of multimodal distribution or bimodal distribution sample affects the detecting sensitivity, this could lead to a deviation from the actual value. In order to identify these differences, we studied particle size distribution of bimodal silica colloids by mixing two mono-dispersed silica colloids having different particle size using DLS and TEM.

## Experimental procedure

### Sample preparation

Eight commercial silica colloids (see table 1) were obtained from Aldrich Chemical and Nissan Chemical Industries. These silica colloids have different particle size and pH respectively. As seen in table 2, bimodal silica colloids were made by mixing two silica colloids having different particle size, M-7 (40 ~ 50 nm) and M-8 (70 ~ 100 nm) with mixing ratio of 2 : 8, 5 : 5 and 8 : 2 respectively. These silica colloids were diluted to 5.0 wt% with distilled water adjusted by pH using KOH and HCl for DLS measurement and TEM sampling.

### Characterization

We have observed colloidal silica particles through transmission electron microscopy (JEM-2000, JEOL) operated at 200 keV. Silica colloids were dispersed for 10 minutes using sonication after dilution to 5 wt%. Samples for TEM measurement were prepared by placing one drop of diluted colloidal silica on the TEM grid placed on filter paper and drying the grid in an oven at 60 ºC for at least 6 hrs. Then the samples were observed at x10K ~ x500K magnification. The particles were observed in bright field images and magnifications showing at least 100 ~ 200 particles according to the particle size to construct a representative particle size distribution. Mean particle size and particle size distribution in TEM image was automatically analyzed by the image analyzer software (Mac-View version 4.0, Mountech Co.). Size distribution can be different according to observation positions. So we have observed from 16 different positions in a TEM grid. Samples diluted to 5 wt% from concentrated silica colloids were measured under constant temperature 25 ºC by dynamic light scattering (DLS) instrument (ELS-Z, Otsuka electronics). The analyzer measures the time-dependent fluctuations in the intensity of scattered light. These intensity fluctuations allows the establishment of an autocorrelation function to determine the diffusion coefficient of particles, which is then converted into a hydrodynamic diameter of the particles, based on the Stokes-Einstein relationship. Mean particles size of each sample is an average of four measurements. [7, 8]

The $D_{BET}$ was calculated by the following equation assuming the spherical particle shape. [7, 9]

$$D_{BET} = 6000/(\rho_p \, SSA) \quad (1)$$

$\rho_P$ is the density of the material (silica, 2.2 g/cm$^3$), SSA is the specific surface area (m$^2$/g) determined by BET analysis. The samples were dried by IR drying and passed through 325 mesh sieve The powder was then outgassed at 200ºC for 2 hrs under vacuum in the degas port.

## Results and discussion

### Particle size of mono-dispersed colloidal silica

We studied the mean particle size of commercial silica colloids using TEM image analysis, DLS analyzer and BET measurement. The results were compared with one another.

Table 1 shows mean particle sizes measured by TEM, DLS and BET analysis over 8 different samples. The particle size from TEM, DLS and BET is named $D_{TEM}$, $D_{DLS}$, and $D_{BET}$, respectively. As shown in Fig. 1, mean particle sizes have different values according to the measurement methods. Except M2 and M6 sample, all the other samples in $D_{DLS}$ indicate larger mean particle size than $D_{TEM}$ or $D_{BET}$. DLS analysis is solution-based method, while BET and TEM analysis are using dried samples. Thus, $D_{DLS}$ can be attributed to the facts that this method measures the size of particles under Brownian motion. Thereby $D_{DLS}$ gives mean hydro-dynamic size which is usually larger than $D_{BET}$ or $D_{TEM}$ as it includes a few solvent layers. Especially, in cases of M-3, M-4 and M-5, DLS measurement value of these samples were significantly higher than $D_{TEM}$ and $D_{BET}$. These samples can be influenced by particle aggregation. [10] M-3, M-4 and M-5 were surface treated for stability and we considered that this treatment led to aggregation formation of particles in solution state. Fig. 2 shows curves and span of the particle size distribution measured by DLS over M-3, M-4 and M-5. SPAN is defined as the following equation.

$$SPAN = (D90 - D10)/D50 \quad (2)$$

Where, D10, D50 and D90 are the particle size at 10%, 50% and 90% of the cumulative volume, respectively. A high SPAN value indicates a wide size distribution. Even though the particles size observed by TEM is similar among M3, M4 and M5 samples, the magnitude of span varies due to the difference in aggregation formation process. In case of M-3 sample, Viota et al. and Vo et al. reported similar DLS analysis results. [11, 12].

Except for M-3 sample, the rest of the samples were observed relatively small through $D_{BET}$ than $D_{TEM}$. This is because there are chances for contraction or pore formation to occur during drying and degassing of sample for BET measurement. So, $D_{BET}$ can be affected by particle morphology and surface conditions. According to A.B.D. Nandiyanto, $D_{BET}$ of mesoporous materials can be considerably smaller than $D_{TEM}$. [13]

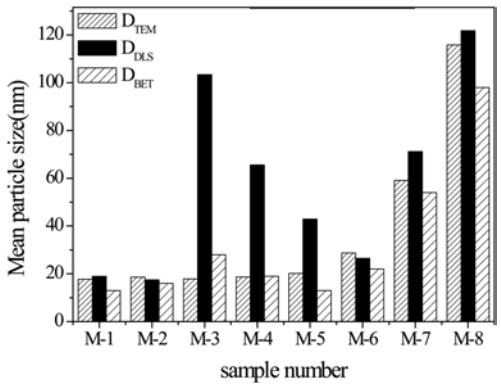


**Fig. 1.** Mean particle size of colloidal silica sol.

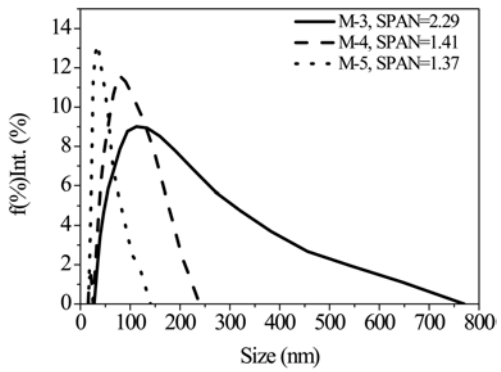


**Fig. 2.** Particle size distribution and SPAN measured by DLS on M-3, M-4 and M-5.

### Particle size distribution of bimodal colloidal silica

We prepared bimodal silica colloids by mixing M-7 and M-8 with different ratios. Table 2 shows the sample name and mean particle size of these samples according to mixing ratio. Fig. 3 shows the TEM images of bimodal samples used for measurement of mean particle size and particle size distribution. Out of the many images, we have chosen well-dispersed silica particles in order to analyze images of the particles accurately.

In the TEM measurement, we confirmed that the particle size distribution of bimodal samples was clearly bimodal and this result matched well with

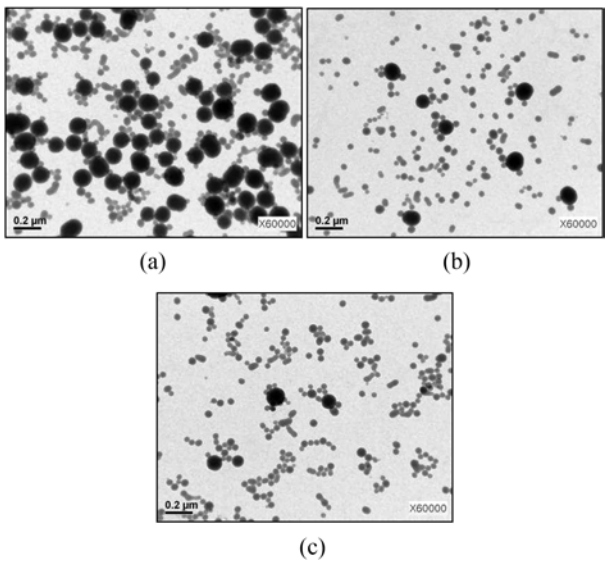


**Fig. 3.** TEM images of bimodal silica colloids : (a) B-1, (b) B-2 and (c) B-3.

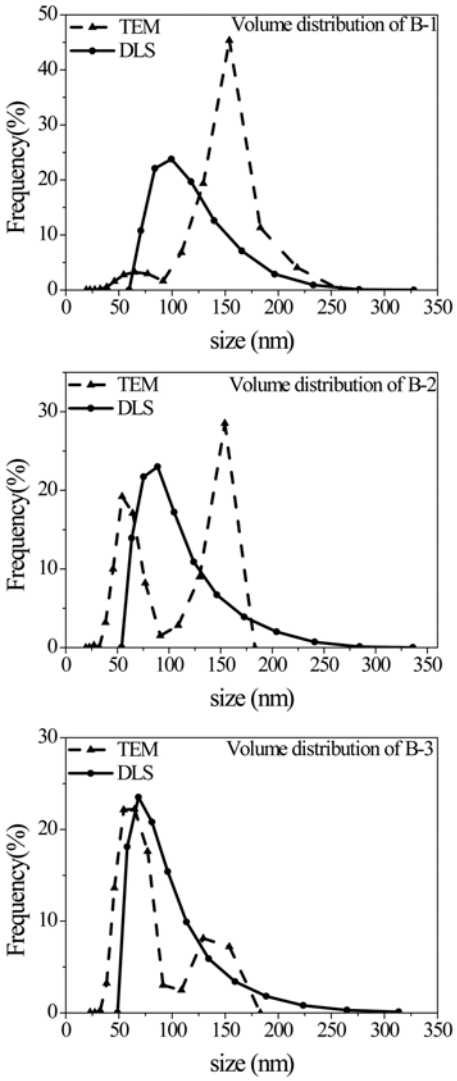


**Fig. 4.** Particle size distribution of bimodal silica colloids by TEM and DLS : (a) B-1, (b) B-2 and (c) B-3.

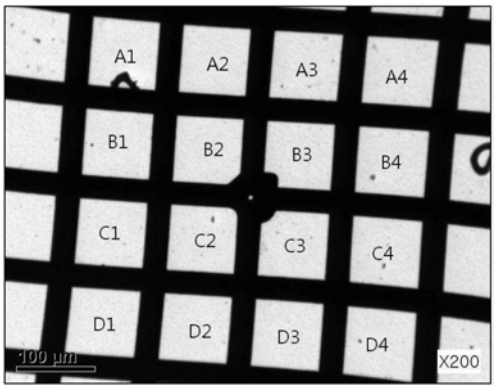


**Fig. 5.** TEM Image of observation positions in a TEM grid of B-3 sample.

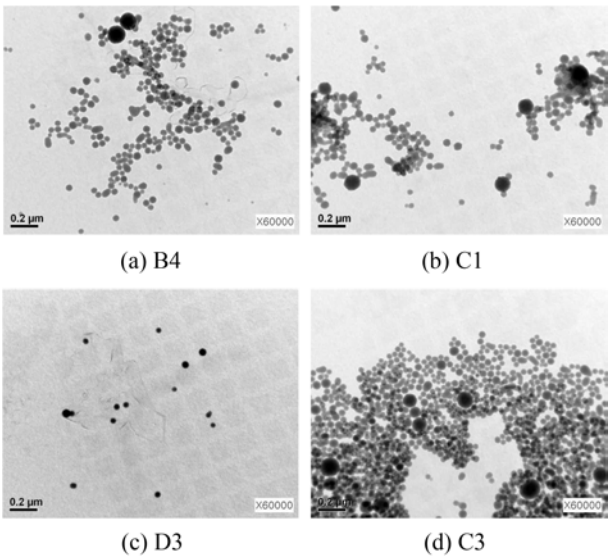


**Fig. 6.** TEM Image of B4, C1, D3 and C3 position in a TEM grid of B-3 sample.

mixing ratio as expected. Particle size distribution of bimodal samples was also measured by DLS method and Fig. 4 shows the graphs of these volume size distributions with TEM and DLS. Unlike the TEM image analysis, bimodal distributions could not be obtained using DLS method due to differences of scattering intensity between large particles and small particles. The scattering intensity of large particles is significantly larger than the intensity of small particles because the scattering intensity of the particles is proportional to the sixth power of spherical particle radius r according to Rayleigh's approximation. So, scattering intensity of large particles contributes significantly to the DLS measurement, while the scattering intensity of small particles is lost in the background signal. [14, 15] In addition, $D_{DLS}$ is larger than $D_{TEM}$ because DLS analysis measures the hydrodynamic diameter of hydrated particles.

In the TEM study using bimodal samples, mean particle size and distribution can be different according to observation positions. Out of the numerous particles on the grid, the TEM image shows only a small fraction. Therefore, TEM method may not be a thorough and accurate representation of the real samples. To prevent this problem, TEM method should analyze sufficient number of particles. Song et al. recommended that the number of particles for the estimation of the Particle size distribution has to be at least 100. [16]

We studied measurement of mean particle size and distribution using TEM according to observation positions. Fig. 5 shows 16 positions on TEM grid of B-3 sample. Fig. 6 shows some TEM images of these positions. Fig. 6(a) is the image of particles relatively well-dispersed. In this case, we could obtain the similar particle size distribution result to mixing ratio. Fig. 6(b) shows that the bigger particles are observed more than the smaller particles. On the contrary, there are no bigger particles in Fig. 6(c) and $D_{TEM}$ measured by this image is considerably small compared to other images. Moreover, the reliability of this image is very low because the number of particles observed in this image is less than 20. Fig. 6(d) is the image affected by

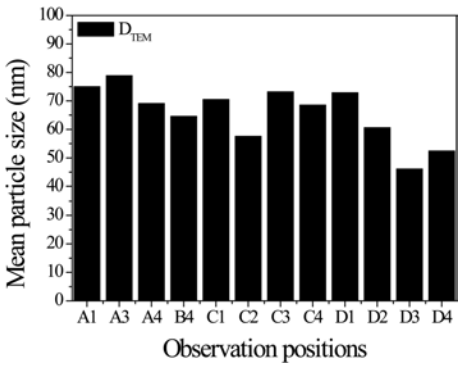


**Fig. 7.** Mean particle size obtained over observation position of B-3 sample.

particle aggregation. As discussed in the previous section, image analyzer software identifies the aggregate as one particle instead of recognizing the aggregate into individually separate particles.

The detection range of the particle size was 20 nm ~ 150 nm in this measurement. Thus, many particles were not counted because large aggregate were calculated to be one particle through image analyzer even though the large aggregate having the size above 150 nm was actually consisted of many particles. We compared $D_{TEM}$ values measured at these positions and showed the standard deviation of these results in the Fig. 7. $D_{TEM}$ may be different according to the observation positions and standard deviation of measured $D_{TEM}$ was about 15%. There are no results for A-2, B-1, B-2 and B-3 positions because there were no particles in these observation positions.

## Conclusion

We have investigated three methods which were used for measuring the mean particle size and particle size distribution of colloidal silica. TEM and BET analysis provided accurate mean particle size of mono-dispersed samples. On one hand, DLS analysis provided slightly large mean particle size compared to TEM and BET analysis. Especially, some samples were shown significantly large mean particle size by DLS analysis because these samples had aggregates in the solution state. For the bimodal samples, TEM image analyzer provided the bimodal distribution consistent with the mixing ratio of colloidal silica. In contrast, DLS analysis failed to detect bimodal distribution in all bimodal samples because the scattering intensity of the particles is proportional to the sixth power of spherical particle radius. TEM and BET analysis provide reasonable results for the mono-dispersed silica sols. The methods take longer time for sample preparation and measurement than DLS. DLS analysis may be the most efficient method available for colloid particle size determination if it is not concerned to determine the primary particle size. In the bimodal samples, if we can obtain the images of well-dispersed particles, TEM analysis is good method for the analysis of bimodal samples.

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