A Technique for Measuring Broad Size Ranges of Aerosol Particles by the Laser Beam Scattering Method Combined with Condensation Nuclei

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Abstract

In order to determine broad ranges of particle size distribution, a new measuring method combined both light scattering and electrostatic separation-condensation nuclei is experimentally investigated. From the experiments, it is confirmed that by using a sensitive optical particle counter connected to a digital computer system, the particle size range of 10 nm to 10 μm in diameter is adequately measurable. Furthermore, using the same criteria to count the number of particles over the entire size range, this method is found to be remarkably applicable as a practical means of more accurate measurement.

1. Introduction

The measurement of particle size distributions dispersed in the atmosphere is usually performed by several different methods, such as optical diffraction, elastic or quasi-elastic light scattering, inertia impaction, electrostatic mobility analysis, diffusion battery, dark-field microscopy, and others. However, there is a basic limitation at approximately 0.1 μm and 1.0 μm in diameter which originates from each measuring principle and occurs in the measurable ranges of particle sizes and concentrations. Due to this, it has been suggested that a technique combining the above mentioned methods might be useful in extensively expanding the measurable size ranges from 1 nm to 10 μm.

In some cases, these combinations cause practical difficulties in adopting the data reduction of the experimental results obtained from each method, because of the different size bases of the particles. It should also be noted that the quasi-elastic light scattering method merely a way to broaden the size of measurement. It seems to be inaccurate for multi-mode particle size distributions.

As a result, a method which combines both sensitive optical particle counting and electrostatic separation-condensation nuclei is experimentally investigated for the purpose of detecting a broad range of sizes between 10 nm and 10 μm in diameter. In practice, particles larger than 0.1 μm are ordinarily measured by the optical particle counter. On the other hand, particles less than 0.1 μm are first separated into a certain narrow size range by the electrostatic force using a differential mobility analyzer, and then the separated particles are increased in size using condensation nuclei in order to count the number of particles. In either case, the number of particles of each size are measured by the same optical counting system, and the size distribution is then obtained in the number-size base. It should be noted again that a more sensitive optical particle counter such as that mentioned above is necessary to employ this method.

Even though this kind of combination might in principle be applicable for the measurement of aerosol particles having a broader size range, there have not been any adequate investigations to experimentally verify this idea. Therefore, theoretical considerations of this method

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and some experimental results using ambient aerosols are discussed in relationship to the cross-sensitive error, counting efficiency, and the size distribution of the aerosol particles.

2. Theoretical Consideration

Figure 1 shows a schematic diagram of the experimental measuring system which consists of a differential mobility analyzer, condensation nuclei, and a sensitive optical particle counter. Using these instruments, the experimental procedures were divided in two ways at the particle size of 0.1 \( \mu \text{m} \) as follows: The particles larger than 0.1 \( \mu \text{m} \) were directly measured by the sensitive optical particle counter itself. Response curves were obtained for the optical particle counter as shown in Fig. 2. This numerical result indicates the well-known relationships for refractive indices of particles, wavelength of an incident light beam, and geometric optical conditions of the optical particle counter?7. In the smaller size range, electrical signals from the light scattering of aerosol particles become small in order to distinguish the noise from the signals because the scattering intensity is proportional to the 6th power of particle size in the region of Rayleigh scattering.
In the size range of 0.1\(\mu\)m and 10\(\mu\)m, an approximate polynomial equation, shown in Fig. 3, might be employed to determine the particle size from the data of light scattering intensity within an error of 5 percent. This equation is of course strongly dependent upon the refractive index of the aerosol particle, and so the measurable size range of the optical particle counter will usually change with materials of the particle. Moreover, in general, it has been pointed out that this method of approximation could not be applied to larger sized particles in the Mie resonance region. However, from the numerical estimation of the permissible error, it was noticed that the sensitive optical counter which was used in this experiment had a broad measurable size range of 0.1 ~ 10\(\mu\)m with sufficient resolution of the particle size for refractive indices of 1.3 to 1.8\(n\). Therefore, in this experiment, the measurable size range was numerically estimated to be 0.1 ~ 10\(\mu\)m, as mentioned above.

For particles smaller than 0.1\(\mu\)m, it is usually difficult to measure particle size distributions by the light scattering method. One useful way to measure those particles would be to combine both electrostatic separation by the differential mobility analyzer and particle counting after the condensation nuclei, which is performed by the same optical particle counter.

The differential mobility analyzer is a well-known instrument for separating particles much smaller than 0.2\(\mu\)m in relationship to the electrostatic mobility of charged particles. In this procedure, the number of elementary charges on a single particle is the most important parameter for separating a certain size of particle by the applied voltage between electrodes. As shown in Fig. 4, a cross-sensitivity of the particle size based on the number of elementary charges occurs in all size ranges at a fixed applied voltage.\(^9\)
For bipolar charging, such as radioactive neutralization, the distribution of particle charges is induced on each size of particle as shown in Fig. 5. This indicates the difference between modified Fuchs' and Boltzmann equations. It has been noticed that the experimental results agreed better with the modified Fuchs' equation for the average of all particles than with the Boltzmann distribution for particles smaller than 0.1 \( \mu \)m. In this size range, the ratio of the particle numbers having a positive single elementary charge to the total number of particles at the size of 0.1 \( \mu \)m was about 24.1 percent, and the ratios for the double and triple charges were 6.4 and 0.7 percent, respectively. Therefore, if the particle only has a single charge, the particle number should be estimated within an error of 7 percent. For particles larger than 0.1 \( \mu \)m, it is impossible to say this because the charge distribution becomes broad. This means that a certain value of electrostatic mobility no longer determines the particle size itself related to the applied voltage. It was also observed that the contribution of larger particles having many elementary charges was negligibly small.

Another factor in the small size region is the method for the conversion of the real number of particles for a given size in which a correction factor, shown in Fig. 6, is used where the neutralized particles have a charge distribution expressed as a modified Fuchs' equation. For sizes smaller than 10 nm, this correction factor for determining the number of particles became extremely large, and the uncertainty in determining particle numbers may have increased. Moreover, the condensation efficiency of these particle sizes became smaller than unity in the nuclei chamber. Therefore, judging from both the technique for counting the loss of particles by the light scattering method and the condensation efficiency of particles smaller than 10 nm, it may be reasonable to apply this correction factor to conversions for counting the number of particles under the limitation that particle sizes are between 10 nm and 0.1 \( \mu \)m in diameter.

According to these considerations, it was theoretically concluded that this proposed method could be applied to the measurement of sizes ranging from 10 nm to 10 \( \mu \)m within an error of 8 percent, and that the number-size.
distributions of particles could be obtained for whole particle sizes. This procedure, which has never been used in practice, would be useful for environmental field work and laboratory studies.

3. The System of Measurement and Procedures of the Experiment

A schematic diagram of the optical unit and signal analysis is shown in Fig. 7. The main measuring devices of this system consist of a particle counter and a wave form analyzer.

Figure 8 shows an on-line measuring system for a laser beam scattering particle counter that was constructed with an He-Ne gas laser of 20mW having a wavelength of 632.8nm (Toshiba, LAG-20), a parabolic mirror for focussing the scattered light, a high speed photoelectric amplifier (Eiko Electric, PEA-HCA using a side-on type photo-multiplier supplied by Hamamatsu Photonics, R928), and data memory with the large size of 256KB (Nippon Kanomax, Model-5211) in order to analyze the pulse height of scattering signals.

The light scattered by the aerosol particle from the laser beam was gathered by a parabolic mirror and then transferred to the photoelectric amplifier through a glass fiber (Nippon

Fig. 7 Schematic diagram of the optical unit and signal analysis

Fig. 8 Flow chart of software for data reduction
Itagarasu, core size of 200 μm and multimode with selfoc micro lens). After that, the scattering signal was stored in the data memory through an A/D converter (Nippon Kanomax, Model-1414, input range of ±2.5V and 10 bit/word) in order to analyze the pulse height for measuring the diameters and concentrations of the aerosol particles by the digital computer system (Nippon Kanomax, Realex-16). A software technique for this data analysis consisted of noise cancelling and counting of the particle number, which were performed in the size range between 0.1 μm and 10 μm in diameter. A wave form analyzer (Analogic, Data-6000, with a sampling rate of 36 MHz) was used to check the shape of the scattering signals.

The same data analysis was applied to measure the size distribution of particles smaller than 0.1 μm. After condensation nuclei, the smaller particle became large, and the numbers for each given particle size which were separated by the differential mobility analyzer were detected by means of the optical particle counter. The scanning of this particle size was performed over several particle sizes by changing with the applied voltage between the electrodes. In this experiment, it was noticed that the S/N ratio of the scattering to the noise signals was extremely high. In order to measure the broaden distribution of particle size, the voltage applied to a photomultiplier was changed with the size ranges. In spite of those complex procedures by using the combined method, data reduction performed by a software technique was sufficient to obtain the particle size distributions even for the broad distributions. Finally, figures of the size distribution were drawn by a X-Y plotter as one of the output modes.

In the experiments, some sample aerosol particles, such as monodispersed polystyrene latex (Dow Chemical; 0.085 μm, 0.109 μm and 0.913 μm, with a refractive index of 1.595), acrylic acid resin powder (with a mean diameter of 0.37 μm and a geometric standard deviation of 1.17 measured by electron microscopy, and a refractive index of 1.38), and nylon powder (with a mean diameter of 2.6 μm and a geometric standard deviation of 2.17, and a refractive index of 1.41) were used for the calibration of some absolute levels of scattering intensities, in order to check the size distributions in the size region less than 1 μm, and in the range larger than that, respectively. Moreover, the ambient aerosol particle was also employed for a sample having a broad size distribution.

Some other experimental conditions were as follows: The dilute liquid for polystyrene laticies was filtered water. In all procedures, the sampling and sheath air flowrates were constant, 16.7 cm³/s and 83.3 cm³/s, respectively. After neutralizations of the electrical charging of the particles using the radioactive source of ²⁴¹Am, the electrostatic separation of smaller particles was done with the differential mobility analyzer. The applied voltage was set up as a digital value and scanned in a range of 1 mV to 3,000V using appropriate intervals. In the condensation chamber, the n-butyl alcohol was vaporized as a condensed liquid at a constant temperature of 413K, which was controlled by the PID method.

4. Results of the Experiment and Discussion

Measured data for the size distribution of

Figure 9: Particle size distribution of acrylic acid resin powder in comparison to the data measured by the electron microscope method.
acrylic acid resin powder indicated that the mean diameter and the geometric standard deviation were 0.38 μm and 1.13, respectively, as shown in Fig. 9. This was similar to the result of the experiment when using obtained by the electron microscope method. It has also been confirmed that the accuracy of this optical particle counter was sufficient to measure particles larger than 0.1 μm, judging from some previous data on the calibration using polystyrene latices and response curves of the particle size.

The particle size distribution of nylon powder is shown in Fig. 10, and indicates that the results of the experiment were qualitatively similar to the data obtained by the centrifugal sedimentation method (Shimadzu, SA-CP2). These number-mean diameters were slightly different from each other. It was also noticed that the particle number concentration did not agree with the data from the cascade impactor. For samples having a broad particle size distribution, these facts could be fundamentally explained by different bases of measuring principles and by an error which occurred due to the conversion of the volume-mean diameter to a number-mean one. However, the S/N ratio of the scattering signal was extremely high for all experimental conditions despite differences between the volumetric and counting methods. Therefore, it was decided that this optical particle counting method could be used to measure particle sizes up to 10 μm, taking into account the complicated effects of both the accuracy of the response curve in size and of light diffraction on the scattering intensity for larger size of particles.

Ambient aerosol was used, because it has a broad range of sizes. This shows the effectiveness of this combined method in the experiments. The result of the size distribution of the sample particles, shown in Fig. 11, was similar to the data from previous investigations. It was also recognized that the S/N ratio of the scattering signal was high enough, as was the case of nylon powder, and that the connection of the experimental data for the size 0.1 μm was smooth and precise in counting the particle size.
numbers. Therefore, it was concluded that this combined method was effective in the measurement of a broad size distribution of aerosol particles between 10 nm and 10 μm in diameter.

In addition, it might be possible to extend this combined method to sizes smaller than 10 nm when considering the condensation efficiency of such tiny particles, which has been experimentally obtained\(^{11}\). However, if this method is expanded to those smaller sizes, it should be recognized that inaccuracies in the data on particle number concentration will increase with the particle counting loss, because the correction factor becomes excessively large.

5. Conclusion

In order to determine broad ranges of particle size distribution, a new method of measurement which combined both the light scattering and electrostatic separation-condensation nuclei was experimentally investigated by means of a sensitive optical counter connected to a digital signal processor. The number concentration of particles for each size was measured by dividing the counting of the particles in two ways at the size of 0.1 μm. The size distribution of particles was finally obtained by integrating these number concentrations of particles using the on-line measuring system.

In conclusion, the experimental results for some sample aerosols indicated that the particle sizes between 10 nm and 10 μm were reasonably determined in relationship to the S/N ratio of the scattering signal and correction factor of the counting efficiency. Therefore, in comparison to other measuring systems, it should be noted that this combined method is sufficiently accurate and useful in measuring the particle size distribution in the same number-size base.

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