

Method for Evaluating the Behavior, and Characteristics of Particles in a Gaseous Phase
— Control of the Dispersed Nanomaterials —

(Main reference is 'Nanoparticle safety handbook (Japanese)'¹⁾)

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1. Introduction

Nanomaterials--as defined by TC229, the ISO Committee in charge of nanotechnology--are "materials that are no more than 100 nm in one-dimensional size". This is the definition that has been cited by many administrative bodies. However, because this definition does not necessarily represent the existence state of actual nanomaterials, the European Commission has recommended that the state in which nanomaterials are agglomerated, aggregated, or coagulated also be included in the definition. On the other hand, there is no real shared consensus on the degree of aggregation at which a unit is considered to be aggregated unit. In addition, the state at which materials should be classified as nanomaterials has not been determined within actual operation. This paper describes the behavior of particles in a gaseous phase, irrespective of their agglomeration or aggregation form and unconfined by the generally accepted definition of nanomaterials, and the methods for measuring them. The target size of the particles is between approximately 10 nm and 10 μm .

2. Behavior of particles in a gaseous phase

An understanding of which forces particles suspended in air are exposed to and how they behave is essential for knowing how to predict errors during the measurement of airborne particles, how to configure an efficient sampling system, and how to use a filter to collect the particles. There are many documents available on studies of the behavior of airborne particles. For more details, see the corresponding reference documents.^{1,2,7)} The representative forces applied to particles suspended in a gaseous phase are described below.

3.1 Brownian motion

Brownian motion describes the phenomenon of particles moving irregularly (random walk) when the molecules and atoms constituting a medium collide with airborne particles. The mean distance (mean square speed = λ^2) at which particles are diffused by Brownian motion for time " t " is given by expression (1).

$$\lambda = \sqrt{2Dt} \quad (1)$$

D is the diffusion coefficient shown in expression (2). It indicates the degree to which particles are diffused by Brownian motion.

$$D = \frac{C_c k T}{3\pi\eta D_p} \quad (2)$$

In this expression, k indicates Boltzmann's constant, T indicates the absolute temperature, and D_p indicates the particle size. η indicates the viscosity of the medium (in this case air) (atmospheric pressure and air at a temperature of 20°C: $1.8 \cdot 10^{-5}$ kg/(m·s)), and C_c indicates the Cunningham correction coefficient (slip correction coefficient) given in expression (3).

$$C_c = 1 + K_n \left\{ 1.257 + 0.4 \exp\left(\frac{-1.1}{K_n}\right) \right\} \quad (3)$$

K_n is the Knudsen number given in expression (4). It indicates the degree to which the flow field is treated as a continuum.

$$K_n = \frac{2\lambda_g}{D_p} \quad (4)$$

In this expression, λ_g is the mean free path for gas molecules.

It is important to note that the diffusion coefficient is inversely proportional to the particle size and the viscosity of the media, but is proportional to the temperature. Essentially this means that the easier it is for the atoms and molecules composing the medium to move, and the smaller the particles are, the faster they will move in an unspecified direction. Essentially this means that the easier it is for the atoms and molecules composing the medium to move, and the smaller the particles are, the faster they will move in an unspecified direction.

3.2 Gravity sedimentation

The terminal velocity (v_t), or the velocity when the speed at which suspended particles fall (gravity settling velocity) becomes constant, is shown in expression (5).

$$v_t = \frac{C_c D_p^2 (\rho_p - \rho) g}{18\eta} \quad (5)$$

In this expression, the variable g indicates the gravitational acceleration, ρ_p indicates the density of particles, and ρ indicates the density of the medium (air).

The time required for the gravity settling velocity to reach the terminal velocity is called the relaxation time (τ). It is obtained by using expression (6).

$$\tau = \frac{\left\{ D_p^2 \left(\rho_p + \frac{\rho}{2} \right) C_c \right\}}{18\eta} \quad (6)$$

The gravity settling velocity (terminal velocity) increases in proportion to the second power of the particle size. In other words, this means that heavier particles rapidly settle if they are the same in density.

In a general atmospheric environment in which there is no specific airflow for carrying particles, it can be assumed that the movement of most particles is controlled by diffusion movement and gravity settling. The tracking characteristics of particles to the airflow are understood as particle behavior caused by inertia force. The Stokes number (St) described in the sampling chapter is used as a rough indicator. Figure 1 shows the diffusion coefficient, the mean movement distance based on diffusion, the gravity settling

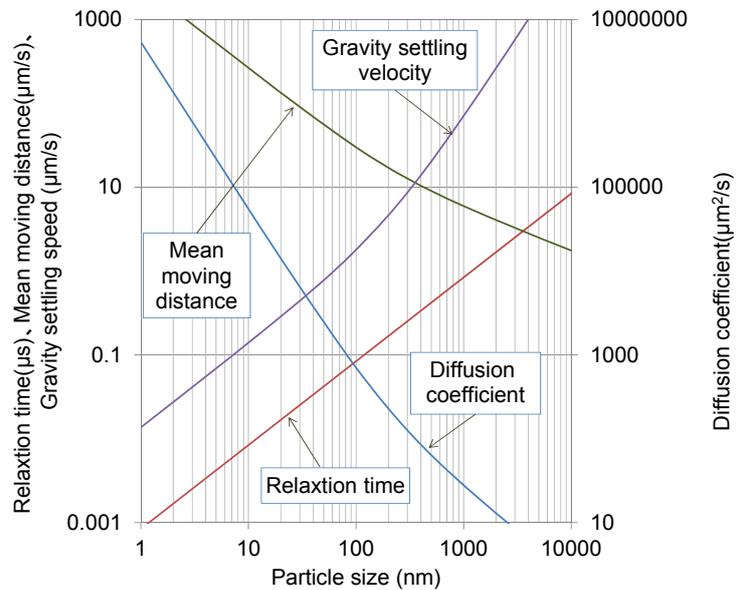


Fig.1 Behavior of particles in a gaseous phase.

velocity (terminal velocity), and the calculated value of the relaxation time, which is the time it takes for the terminal velocity to be reached. Their values are shown on the vertical axis, corresponding to the particle sizes shown in the horizontal axis. These calculations were performed using a globe-shaped particle with a density of 2 g/cm^3 suspended in an atmospheric (density: 1.29 kg/m^3) environment at normal temperature (20°C). Under these conditions and near a particle size of 350 nm, the distance at which gravity causes the particles to settle per unit hour becomes nearly equal to the mean distance at which the diffusion force causes the particles to move per unit hour in a random direction. It is known that a particle of about 300 to 500 nm in size appears to have the same level of influence as gravity and diffusion when the physical properties and environmental conditions of particles suspended in the air are taken into consideration. Particles of less than 300 nm in size are significantly influenced by diffusion force. These particles move at random while they are being carried by the airflow and do not settle easily. For particles larger than 500 nm in size, movement is determined by the influence of gravity. Therefore, these particles in space settle rapidly in the absence of any significant ascending airflow.

If nanomaterials are suspended as primary particles, their behavior can be satisfactorily understood by considering only the diffusion force. In actuality, it has been reported that in a gaseous phase nanomaterials are often suspended in an agglomerated or aggregated state.³⁾ When controlling the exposure risk of dispersed nanomaterials, particles of up to several μm in size must be measured. The concept of particle behavior indicated above is used as an important item of information for equipment configuration when measuring airborne particles for sampling, as well as when checking

the error of the measured value.

3. Measurement of airborne particles

There are various methods for measuring and analyzing nanomaterials. The method used depends on the respective application.³⁾ The following sections describe the measuring equipment used to measure the number concentration of nanomaterials or their aggregated particles, suspended in a gaseous phase, in real time. Until now, APCs (light scattering airborne particle measuring equipment, known as airborne particle counters) and CPCs (condensation particle counters) have been widely used to measure the number concentration of airborne particles in a wide range of environments, from clean rooms, where cleanliness was controlled, to general living environments. The principles and configuration of APC and CPC are outlined below.

3.1 Airborne particle counter

An airborne particle counter (APC) is the general name for a light scattering airborne particle counter. Its basic performance specifications are described in the ISO21501-4 and JISB9921 standards. An APC is easy to operate and comparatively low in price, and because it measures the number concentration and particle size distribution of sub-micron size or larger particles in the air, it is widely used for controlling cleanliness and evaluating the performance of ventilation filters. The size of the smallest particle that can be measured by a general use, portable APC is approximately 0.3 μm . For a high performance, open cavity type APC that uses a laser resonant cavity as the particle detection area, the smallest measurable particle size is approximately 0.1 μm . Consequently, nano size particles cannot be measured directly. However, as described previously, nanomaterials in a gaseous phase often exist in an aggregated state. An APC is ideal for measuring particles, ranging from sub-microns to a few microns in size, which are generated by the coagulation and growth of nanomaterials.

Figure 2 shows an overview of the particle detection schematic of a general use APC. An APC is a system in which particles suspended in the air are sucked up in their suspended state and sent to the particle detection block. When particles pass through irradiated light, a pulse-shaped light-scattering phenomenon is detected. The number of detected pulses corresponds to the number of particles, and the light-scattering intensity corresponds to the

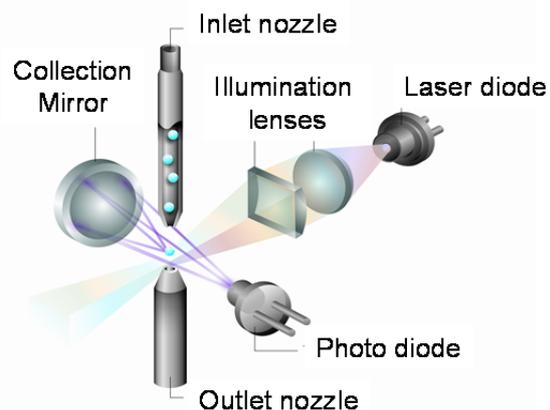


Fig.2 Schematic structure of particle detection system in APC.

size of the particles. The standard for the particle size is the scattered light intensity of the polystyrene latex (PSL) (refractive index: approx. 1.59) particles in the air. Therefore, it must be noted that, if a particle has a different refractive index, the geometrical particle size differs from the measured particle size of the APC.⁴⁾ The correct number of particles cannot be measured when multiple particles exist simultaneously in the particle detection area. Thus, there is a maximum limit on the particle concentration that can be measured by the APC. The corresponding value must be stated clearly in the specifications, as specified in the standards that were previously described. Careful attention must be given when measuring particles in a high-concentration environment.

OECD (Organization for Economic Co-operation and Development) has made the guideline on the dispersion control procedure for nanomaterials available to the public.⁴⁾ This guideline recommends using a handheld APC together with a portable CPC (described later) as the simplified dispersion measurement method of nanomaterials. The basic performance of a handheld APC requires it to be able to measure particles between 0.3 μm and 10 μm in size (with 0.3 μm being the smallest measurable size), and to have a sample flow rate of 2.83 L/min. These performance requirements are satisfied by most general-use APCs which weigh 1 kg or less. Their portability makes them easy to carry and operate at a variety of sites. In many industries, an APC with a sample flow rate of 28.3 L/min has been frequently used as the standard APC for managing clean spaces such as a clean room. In recent years, APCs with a sample flow rate of 50 L/min or more have also been used to control the production environment of sterilized medicines and high-pharmacology active medicines. The dispersing status of nanomaterial (or its aggregated unit) particles can be detected in lower concentrations because the particle contamination environment in the background appears to have a high level of cleanliness that can be controlled by an APC with a high flow rate. The dispersed amount of nanomaterials to be controlled is not necessarily clear at this current point in time. However, controlling the dispersed amount at a higher level of sensitivity is an effective means for lowering the risk. That being said, there is no need to replace the current model for control with a handheld APC or portable CPC.

3.2 Condensation particle counter

When visible light serves as the irradiated light, the reduction in the light scattering phenomenon of fine particles of 100 nm or less in size is in proportion to approximately the sixth power of the particle size. Thus, it is difficult to detect the suspended primary particle-sized nanomaterials by using the light scattering phenomenon. A condensation particle counter (CPC) has been predominantly used in research to measure the number concentration of airborne particles that are 100 nm or less in size. A CPC can be used as a means for introducing sample air, containing particles, into the supersaturated steam atmosphere created when the high-temperature steam of water or alcohol is mixed, condensing the steam into droplets that grow by using the introduced particles as

condensation nuclei, and for measuring the number of grown particles together with an APC. When using a CPC, sample air containing particles is introduced into the supersaturated steam atmosphere created when the high temperature water or alcohol steam. This causes the steam to condense into droplets that grow by using the introduced particles as condensation nuclei. The total number of grown particles is measured using an APC.. An adiabatic expansion type, heating-cooling type, and steam-mixing type can be used to obtain the supersaturated state. At this time, the most widely used type is the heating-cooling type. The heating-cooling type CPC induces the condensation growth of particles in a supersaturated state, which is produced by inserting fine particles into a heated saturator, in which the steam of alcohol or water is in a saturated state, and then rapidly cooling the saturated air containing these fine particles. The CPC condenses and grows particles moving together with the airflow, thereby making it possible to conduct continuous measurements. The limit on the size of condensation growth depends on the balanced degree of the particle surface and ambient steam pressure. Thus, it does not depend on the size of particles that are at the nucleus of growth. As a result, the particle size information is lost unless a classification apparatus, such as a differential mobility analyzer (described later), is used to select the particle size before growth.

The schematic configuration of the condensation growth block and particle detection block in the portable CPC recommended by OECD guidance is shown in Figure 3. The portable CPC does possess functionality for classifying particle size because it is compact and easy to carry. However, it is possible to measure the total number concentration of particles (which can be condensed and grown) of at least approximately 10 nm in size.

The maximum particle concentration that can be measured by a CPC is between approximately 10^3 and 10^4 /mL. There is also equipment on the market which sacrifices portability for effective condensation growth and is capable of measuring particles near up to 3 nm in diameter. However, the deposition loss caused by Brownian diffusion in the equipment has a significant effect on the measured value, and the affinity of the working liquid for fine particles to be measured influences the detection efficiency. Thus, certain consideration must be made for proper particle loss in the equipment and variation in growth probability according to particle size.

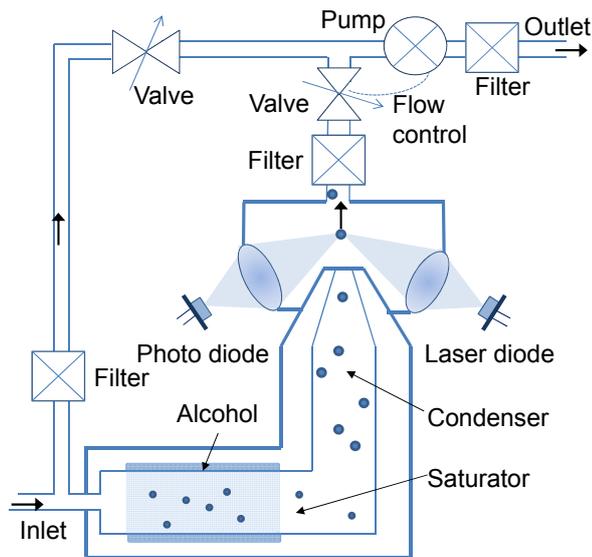


Fig.3 Schematic structure of CPC.

3.3 Differential mobility analyzer

Information about the size of original particles that served as the nucleus of growth is lost when the particles are condensed for growth. For this reason, the particle size must be classified before inserting a sample into a CPC when particle size information is required. A differential mobility analyzer (DMA) is often used as the apparatus for classification. The DMA is an electrostatic classification apparatus that selects the size of particles based on the movement distance caused by the electrical mobility (Z_p) of charged particles, as shown in expression (7).

$$Z_p = \frac{C_c p e}{3\pi\eta D_p} \quad (7)$$

In this expression, p represents the number of electric charges a single particle possesses, while e indicates the elementary electric charge ($= 1.6019 \cdot 10^{-19} \text{C}$)

The DMA is called a differential type because it classifies only particles with electrical mobility that enables them to travel a specified movement distance. An integrating system that measures all particles which do not exceed the specified electrical mobility is called an electrical aerosol analyzer (EAA). The condition for using a DMA to classify particles is that they must all be charged uniformly. Thus, charging equipment that controls the charging state of the particles is installed on the upstream side of the DMA.

3.4 Other measurements

When investigating the impact on human health caused by PM_{2.5} (airborne particle of 2.5 μm or less in sizediameter) and other contamination particles in the air, the mass concentration of particles is generally used as the reference for control. For nanomaterials, the decrease in the particle size causes the mass concentration to become incredibly low. However, it is feared that new health problems will occur if the surface area or particle concentration per unit mass increases. Because the number of particles can be easily measured, the previously described use of APCs and CPCs for particle concentration control is recommended by the relevant ministries, agencies, and international organizations. On the other hand, there are some who believe that the particle surface area should be used as the basis for evaluating nanomaterials because an increase in the surface area per unit quantity causes particles to activate more easily, thereby possibly causing health problems. Measuring the mass of each nanomaterial has also been proposed as a useful means for identifying the characteristics of nanomaterials. The following section provides examples of measurement methods and their intended purpose.

3.4.1 BET-specific surface area measuring equipment

This method applies the BET (Brunauer, Emmett, and Teller) theory—which describes the adsorption phenomenon in a solid-gas interface—to measure the external and internal surface areas

and the specific surface area of particles from the gas quantity physically adsorbed on the particle surface. An inactive gas such as N₂, Ar, or Xe is used as the adsorbed gas. For non-porous and non-sticking nanomaterials and for when primary particles are prescribed in spherical form, expression (8) represents the relationship between the volume-based specific surface area S_V and the mass-based specific surface area S_W , and the specific surface area sphere-equivalent size X_{SV} (also known as the Zuiider size).

$$S_v (= \rho S_w) = \frac{6}{x_{SV}} \quad (8)$$

When measuring a specific surface area, the particle size distribution cannot be obtained because the target object is the total specific surface area of the sampled particle group. In this case, primary particles can be evaluated as the mean primary particle size, even if they form an aggregated state. However, this method cannot be applied to the particles with a composition and shape that absorbs adsorbed gas.

3.4.2 Aerosol particle mass analyzer

An aerosol particle mass analyzer (APM) classifies airborne particles according to their mass (or more precisely, according to their mass/charge count). It can be used to classify particles that are approximately 1 μm or less in diameter. Figure 4 shows the basic classification structure. A coaxial double cylinder is rotated at a high

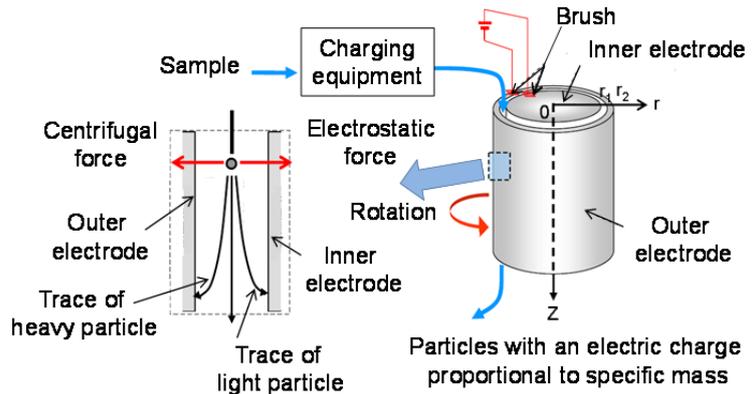


Fig.4 Schematic structure of APM.

speed of a few 1000 rpm, and voltage is applied between the cylinders. When the charged particles are inserted into the clearance, the centrifugal force acts on the particles in the radial direction of an electrode, and the electrostatic force corresponding to the charging state acts in the direction of the electric field. Only particles with a balance between the electrostatic force and centrifugal force pass between the double cylinder electrodes. Consequently, the basis for classification is the mass ratio, which is represented as the ratio of mass to the charged quantity. The balance between the centrifugal force and electrostatic force is shown in expression (9).

$$mr\omega^2 = \frac{qV}{r \ln\left(\frac{r_2}{r_1}\right)} \quad (9)$$

In this expression, m indicates the mass of a particle, r indicates the radius vector coordinate of

the particle, and ω indicates the rotation angle speed of an electrode. V indicates the inter-electrode voltage, r_1 indicates the inner electrode radius, and r_2 indicates the outer electrode radius. Because $r_2 - r_1$ is much smaller than the electrode radius, r can be approximated by using the mean electrode radius ($r_c = (r_2 + r_1)/2$). The ratio m/q of the classified particles is given by the expression (10).

$$\frac{m}{q} = \frac{V}{r_c^2 \omega^2 \ln\left(\frac{r_2}{r_1}\right)} \quad (10)$$

The variables on the right side are determined by the equipment conditions. Therefore, the mass (m) of each individual classified particle is determined by using another method to estimate the charged quantity (q) of the classified particles. This method is used to obtain classified particles according to mass. However, this method is also considered useful for obtaining information on the density or components of particles if the DMA, described previously, is installed on the upstream side of the APM and if the size value of the aerodynamically classified particles is synchronized with the value detected by the DMA.

4 Sampling of airborne particles

Airborne particles are usually passed through a sampling pipe via airflow and then sent to the particle measuring equipment. The following section lists precautions to be observed when using a sampling pipe to conduct measurements. It also explains the underlying concepts for efficient measurement.

4.1 Isokinetic sampling

In an environment where the airflow direction or velocity of ventilation is readily apparent, such as a unidirectional airflow clean room, the optimal method for measuring airborne particles is isokinetic sampling. In this form of measurement, the sampling pipe is opened in the direction opposite to the airflow direction of the air conditioning, and then the sampling

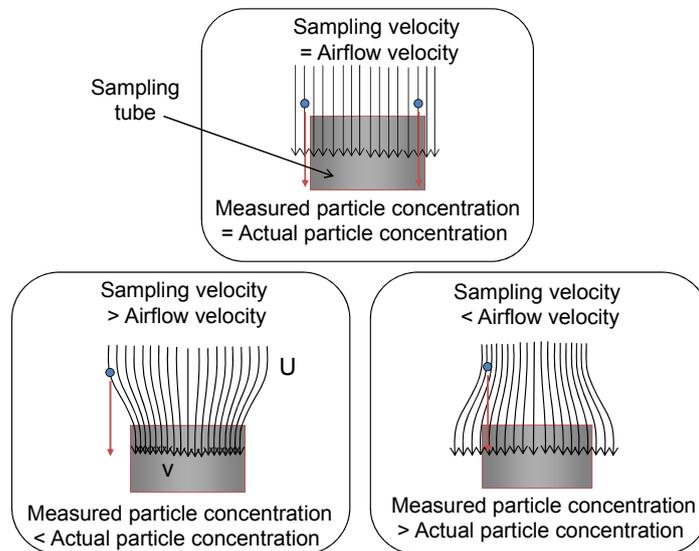


Fig.5 Isokinetic and un-isokinetic sampling.

essentially this means that the easier it is for the atoms and molecules composing the medium to move, and the smaller the particles are, the faster they will move in an unspecified direction. Velocity of the sampling pipe's opening is made the same as the airflow velocity of the ventilation. Figure 5 shows an image of the isokinetic sampling and unisokinetic sampling. When the sampling

velocity is higher than the airflow velocity, particles cannot follow along the flow line in the sampling pipe, and the number of particles to be measured becomes smaller than the actual number of particles. When the sampling velocity is lower than the airflow velocity, particles cannot follow the flow line leading out of the sampling pipe, and particles that should not be counted flow into the sampling pipe. As a result, the number of particles to be measured becomes larger than the actual number of particles. The followability of particles to a flow line are dependent on the inertia force of particles. The actual influence of unisokinetic sampling on the measured value has been researched often in experiment and theory. In this case, Durham and Lundgren calculated the degree of influence by using expression (11)⁶⁾, which they obtained through an experiment.

$$\frac{C_s}{C_o} = 1 + \left(\frac{U}{V} - 1\right) \left\{ 1 - \frac{1}{1 + \left\{ 2 + 0.62 \left(\frac{V}{U}\right) \right\} S_t} \right\} \quad (11)$$

In this expression, C_o indicates the actual particle number concentration, C_s indicates the particle number concentration to be sampled, and U indicates the airflow velocity. V indicates the sampling flow velocity, and S_t indicates the Stokes number of particles. The Stokes number is a dimensionless number that indicates the inertia force level of particles. It is given by expression (12).

$$S_t = \frac{D_p^2(\rho_p - \rho)C_c U}{9\eta d} \quad (12)$$

In this expression, d is the typical length of the flow field. The size of the sampling pipe is used in this case. Figure 6 shows the calculation result of a measurement error caused by unisokinetic sampling, in which the particle size serves as the parameter. The horizontal axis indicates the diameter of the sampling pipe. The vertical axis indicates the ratio of the concentration of measured particles (particles sucked into a sampling pipe) to the actual particle concentration. The unisokinetic sampling is obtained when the diameter of a sampling pipe's opening is 11 mm because an ambient airflow of 0.5 m/s and a sampling flow rate of 2.83 L/min were prescribed. When a particle of 1 μm or less in size is targeted for measurement, no significant influence of counting caused by unisokinetic sampling is observed, even if the ratio of the flow

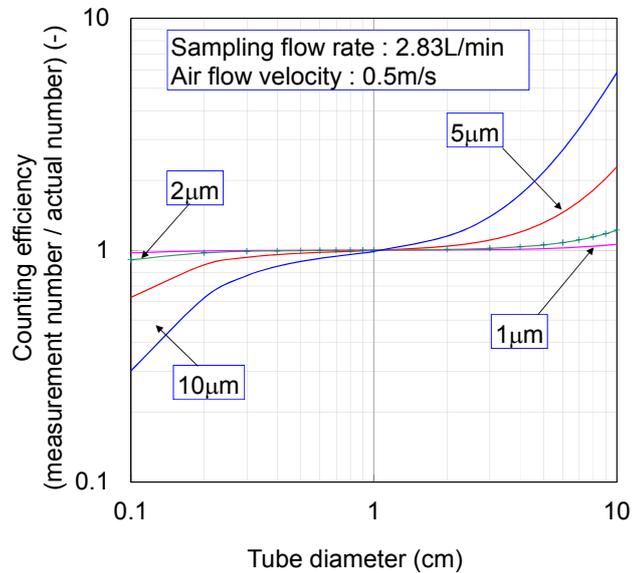


Fig.6 Measurement error caused by un-isokinetic sampling. (particle density : 1g/cm^3)

velocity changes approximately 100 times. Thus there is believed to be no need to accurately maintain isokinetic sampling. However, isokinetic sampling must be taken into consideration when controlling coarse particles, such as aggregated particles, of a few μm or more in size.

4.1.1 Direction of the sampling pipe opening

In an environment where the direction of airflow is difficult to determine, such as a nonunidirectional airflow clean room, the measurement conditions are generally made consistent by turning the opening of a sampling pipe upwards. When the sampling pipe is not opened in the direction opposite to the airflow, the influence exerted by the angle between the sampling port direction of the sampling pipe and the airflow direction on the sampling efficiency can be obtained by the Durham and Lundgren experimental expression (13)⁶⁾.

$$\frac{C_s}{C_0} = 1 + (\cos \theta - 1) \left\{ 1 - \frac{1}{1 + 0.55S'_t e^{0.25S'_t}} \right\} \quad (13)$$

In this expression, $S'_t = S_t e^{0.22\theta}$. θ indicates the gradient of the sampling pipe's opening toward the airflow direction.

Expression (13) can be applied within the range of $0.01 < S_t < 6$. When the density of particles is high ($S_t > 6$), the counting loss caused by the inclination of the sampling pipe is represented by $\cos(\theta)$. For $S_t < 0.01$, the inertial movement of particles can be ignored, and thus no significant counting loss is considered to be caused by the gradient.⁷⁾

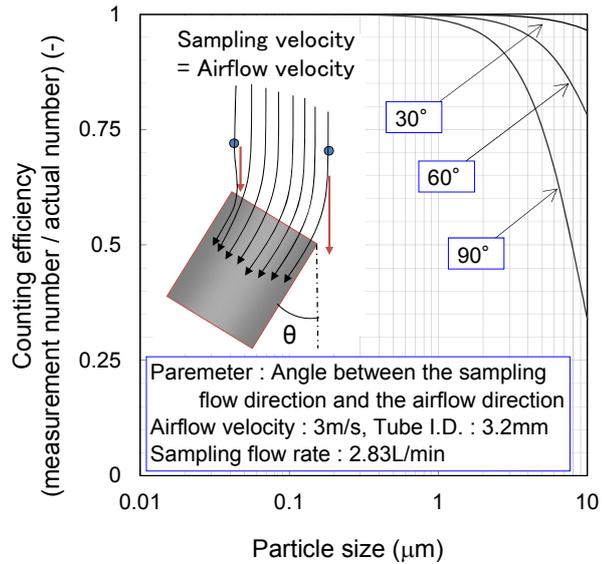


Fig.7 Sampling coefficient by inclined sampling port. (Particle density : 1g/cm^3)

The calculation result obtained by using expression (13) is shown in Figure 7. The calculation is performed under conditions in which a sampling pipe with an inner diameter of 3.2 mm (1/8 inch) was used to suck the particles at a flow velocity of 2.83 L/min (0.1 cfm) from airflow of 3 m/s. The sampling velocity of the sampling pipe is about 5.9 m/s. The speed at which the particles are sampled is about two times as high as the airflow velocity. The counting ratio is controlled by the particle behavior generated by inertia force. Therefore, it approaches 1 when the airflow velocity decreases or when the sampling velocity increases. It is known that the sampling angle exerts little influence on the measured value, even if a particle of $1\ \mu\text{m}$ or less in size is sampled in the direction orthogonal to the airflow

direction.

4.2 Length and inner diameter of the sampling pipe

In a process in which particles are carried through a sampling pipe, the efficiency at which the particles pass through the sampling pipe decreases when the particles are deposited and adhere to the inner wall of the pipe. As a result, the evaluated particle concentration may be lower than the actual concentration. The deposition mechanism of particles carried together by an airflow is mostly understood by gravity settling, inertial deposition, diffusion deposition, and electrostatic deposition. Inertial deposition can be reduced by preventing the tight bending of the sampling pipe, increasing the ratio of the typical length of the fluid to the particle size, and decreasing the S_t number (expression 12). Under ordinary measurement conditions, there is no noticeable influence because particles of 1 μm or less in size are considered to follow the airflow.

On the other hand, diffusion deposition and gravity settling cannot be prevented when a long sampling pipe is used. Diffusion deposition becomes noticeable as the particle size decreases. Gravity settling exerts a greater influence because of the large particles. The particle deposition rate (C_d) resulting from Brownian diffusion

in the horizontal circular pipe is obtained by using the Gormley & Kennedy expression (G-K expression)⁸⁾, which is shown in expressions (14) and (15). The particle deposition rate (C_g) resulting from gravity settling in the horizontal circular pipe can be obtained by using the Natanson & Thomas expression⁹⁾ shown in expression (16). Figure 8 shows a calculation example of particle loss caused by diffusion deposition and gravity settling in the sampling pipe. The results are obtained by using the G-K and Natanson & Thomas expressions.

$$\text{For } \mu < 0.07, C_d = 1 - 5.50\mu^{2/3} + 3.37\mu \quad (14)$$

For $\mu > 0.07$,

$$C_d = 0.819 \exp(-11.5\mu) + 0.0975 \exp(-70.1\mu) + 0.0325 \exp(-179\mu) \quad (15)$$

However, $\mu = \frac{4DL}{\pi d^2 U}$

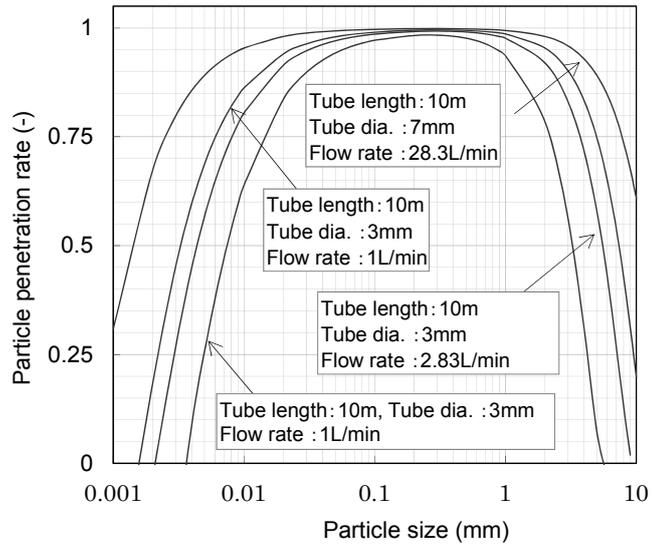


Fig.8 Particle loss characteristic in sampling tube.
(Horizontal placement)
(Particle density: 1g/cm^3)

In the last expression, L indicates the piping length, d indicates the pipe diameter, and U indicates the flow velocity. The means for obtaining the settling rate (C_g) resulting from gravity is given by expression (16) below.

$$C_g = \frac{2}{\pi}(\alpha\beta + \sin^{-1} \beta - 2\alpha^3\beta) \quad (16)$$

In this expression, $\alpha = \left(\frac{3v_t L}{4DU}\right)$ and $\beta = \sqrt{1 - \alpha^2}$

The passage rate characteristics of the particle sampling pipe shown in Figure 8 are obtained by combining each result. Many reports show that a good correlation is obtained between the calculating expressions and measured values when the particle behavior is controlled by diffusion deposition and gravity settling. The maximum sampling flow rate of commercially available CPCs is about 1 L/min. The passage rate of a particle with a size of 100 nm or less, resulting from diffusion deposition, decreases remarkably when a 10 m sampling pipe with an inner diameter of 3 mm is used to sample the particles at a flow rate of 1 L/min. The passage rate of particles with a size of 10 nm is 65% or less, and that of particles with a size of 5 nm is 10% or less. The latter rate shows that very few particles pass through. Even when the sampling pipe is shortened to 2 m, a passage rate of only 85% is obtained for particles with a size of 10 nm. For particles with a size of 5 nm, a passage rate of about only 70% is obtained. The particle passage rate in a pipe is calculated to be about 95% for particles with a size of 10 nm when a 10 m sampling pipe (with an inner diameter of 7 mm) is used to suck the particles at a sampling flow rate of 28.3 L/min. Even for particles with a size of 5 nm, the particle passage rate is calculated to be about 90%. This shows that an increase in the flow rate in a sampling pipe is an effective means for improving the passability of particles.

Gravity settling is considered to be dominant for particles with a size of 1 μm or more. In controlling the dispersion of nanomaterials, the sampling flow rate of the portable APC recommended for measuring particles with a size of 0.3 μm or more is predominantly 2.83 L/min. A passage rate of 95% or higher is obtained for particles with a size of 1 μm when a 10 m sampling pipe with an inner diameter of 3 mm is used to sample the particles at a flow rate of 2.83 L/min. However, the passage rate is only about 60% for particles with a size of 5 μm . A passage rate of 80% or more can be secured for 5 μm

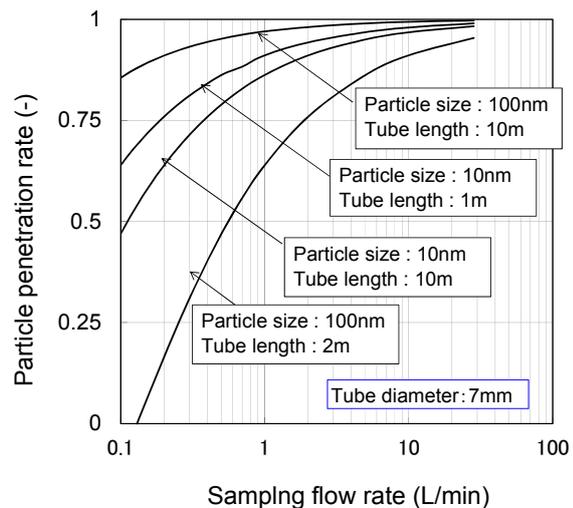


Fig. 9 Nano size particle penetration rate characteristics in sampling tube.

particles by specifying a flow rate of 28.3 L/min.

4.2.1 Sampling of particles smaller than 100 nm in size

As described previously, particle loss caused by diffusion deposition becomes noticeable when a particle of 100 nm or less in size is treated for measurement. Figure 9 shows an example of calculating the relation between the sample flow rate and particle passage rate when a 10 m sampling pipe with a pipe diameter of 7 mm is used. For particles with a size of 100 nm, a passage rate of 90% or more can be secured even when a flow rate of 0.2 L/min is specified. However, for particles with a size of 10 nm, it is known that a passage rate of 90% cannot be obtained when the sample flow rate is below 10 L/min. When a sampling pipe a few meters or more in length is used to sample the particles to be measured, the degree of particle loss is dependent on the length of the sampling pipe and the flow rate. In short, this means that particle loss is dependent on the amount of time particles are in the pipe. Therefore, it is best to shorten the length of the pipe as much as possible and carry samples at a high flow rate (with a flow rate of roughly 28.3 L/min). However, the acceptable flow rate for CPCs that measure particles with a size of 100 nm or less is about 1 L/min, so the sampling system needs to be designed to carry particles at a high flow rate right up to the measuring equipment and then branch the sample flow.

4.2.2 Sampling of particles larger than 1 μm in size

Gravity causes large particles of several μm or more in diameter to settle rapidly. Figure 10 provides an example of calculating the settling loss of particles 1 μm or larger in a sampling pipe that is positioned horizontally. To obtain the particle loss, which is dependent on the inner diameter of the sampling pipe and the sampling flow rate, a 5 m sampling pipe is used. Even though the sampling pipe is only a few meters in length, significant particle loss occurs if the particles are not sucked at a flow rate of at least 28.3 L/min or more. The influence of gravity can be eliminated by positioning the sampling pipe vertically. When the sampling pipe is positioned horizontally, it is necessary to understand the measured value based on that particle loss exceeding a certain amount occurs necessarily.

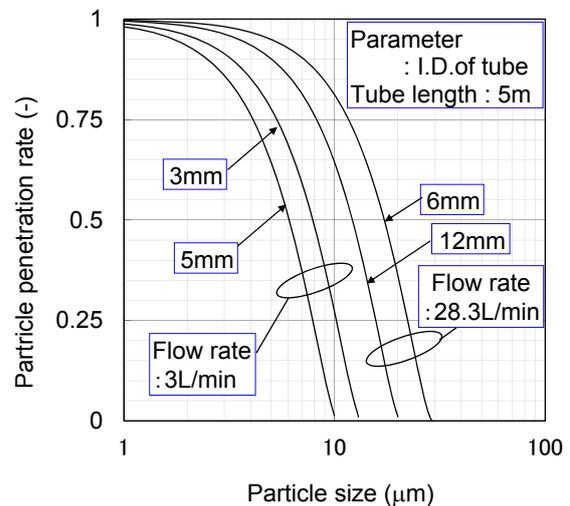


Fig. 10 μm-size particle penetration rate characteristic in sampling tube.

4.3 Material quality of the sampling pipe

In general, it is easy to negatively charge particles suspended in the air. A number of suspended states are considered when nanomaterials are dispersed in the air, such as nanomaterials, the coagulated bodies of nanomaterials, and coagulation with general suspended particles. However, since it is assumed that the charging state is largely the same as that for general particles in the air, the passage rate of particles is believed to decrease when a charged sampling pipe is used. Figure 11 shows an example of an experiment in which several kinds of sampling pipes were forcibly charged to measure each individual particle passage rate.¹⁰⁾ The sampling pipes, each 300 mm long and with an inner diameter of 5 mm, were installed in the electrodes of a parallel flat plate. The voltage between the electrodes was scanned and the charging quantity of each sampling pipe was changed. A PSL particle with a size of approximately 0.5 μm was carried at a flow rate of 500 mL/min to measure the number of particles on the upstream and downstream sides of each sampling pipe and obtain the passage rate. Elicon is a trademark of a commercial antistatic tube used here. In a conductive SUS tube, the particle passage rate depends very little on the electric field strength. In regards to the non-conductive materials used for the experiment, materials with a lower dielectric constant exhibit have higher insulation characteristics. Therefore, there is a noticeable decrease in the particle

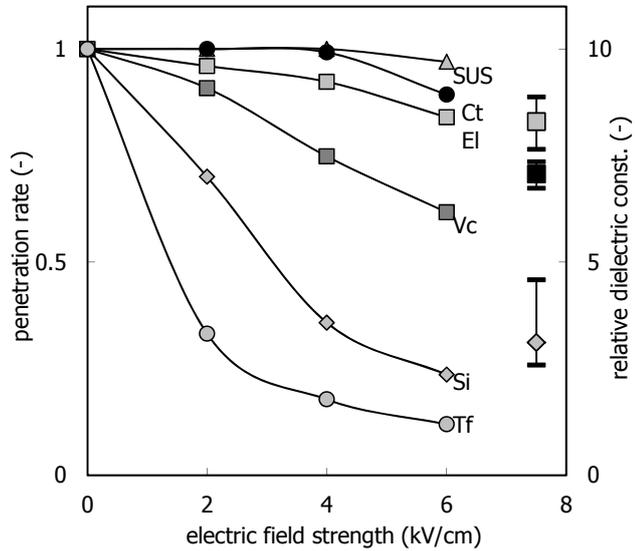


Fig. 11 Particle penetration characteristic dependent on the material of the sampling tube. (SUS : stainless, Ct : conductive tube, EL : Elicon, Vc : Vinyl chloride, Si : Silicon, Tf : Teflon)

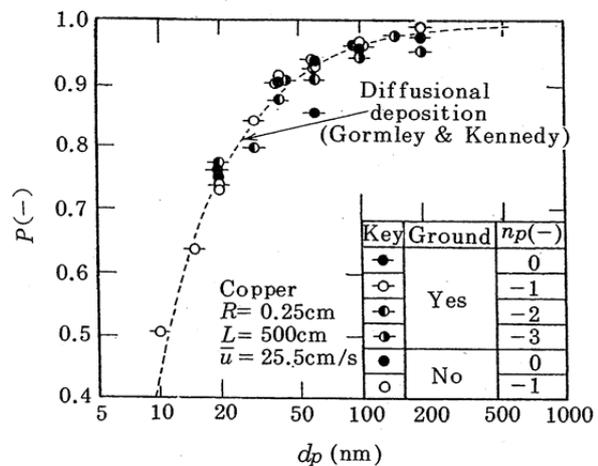


Fig.12 Particle penetration characteristic of a copper tube.

passage rate for silicon tubes and Teflon tubes.

For particles with a size of $0.2 \mu\text{m}$ or less for which the particle loss caused by gravity settling can be ignored, it is known that the consistency of the particle passage rate based on the Brownian diffusion obtained by the G-K expression (expressions (14) and (15)) with the measured value varies according to the material quality of the pipe.¹¹⁾ Figure 12 shows the passage rate of particles in a copper tube, and Figure 13 shows the passage rate of particles in a PMMA (polymethylmetacrylate, acrylic resin) tube. The test particles are made

up of NaCl, and the charge number n_p is controlled from an uncharged state to 3. Because the copper tube is conductive, there is no electrostatic force acting between the tube wall and particles, regardless of the charged state of the particles. Thus, because the only factor controlling the loss of the particles is Brownian diffusion, the G-K expression and the measured value, which does not account for electrostatic precipitation, are largely consistent. The glass tube acts as an insulator, but it exhibits a comparatively high dielectric constant. As a result the electrostatic potential decreases, there is little electrostatic deposition of particles, and particle loss resulting from Brownian diffusion becomes dominant. There is little difference between the result obtained through the experiment and the value of the G-K expression. In a pipe made of a high-polymer material such as acrylic resin, the surface electrostatic potential increases easily and there is a noticeable occurrence of particle loss in the charged particles caused by the influence of electrostatic precipitation. There is a tendency for the obtained result to differ significantly from the value of the G-K expression. Particle loss caused by electrostatic precipitation increases in an insulated sampling pipe made of material with a low dielectric constant. The use of these types of sampling pipes should be avoided.

5 Conclusion --Distinction from particles in the background--

To measure and control the nanomaterials dispersed in the air, the natural particles existing in the background must be distinguished from the nanomaterials. To do this, it is important to determine the size range in which measured particles can be easily distinguished, based on the assumption that nanomaterials are dispersed in a coagulated state. In practice, the range is determined by examining work processes or equipment that may potentially disperse nanomaterials and comparing the difference in particle size distribution during operation and while at rest. In a space where the level

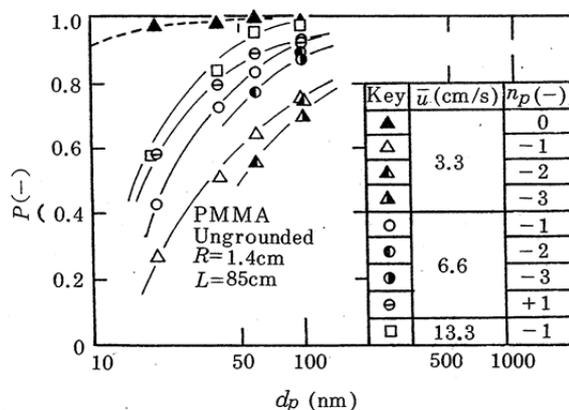


Fig.13 Particle penetration characteristic of a PMMA tube.

of cleanliness or air conditioning is controlled, such as a clean room, it is easier to determine the existence of dispersed nanomaterials and their particle size. However, in a space that resembles the conditions of a normal environment, which is affected by time zones and the elements, it may be necessary to determine the existence of dispersed nanomaterials or their particle size based on the accumulation of a measured value and the statistical processing.

The absence of primary particles or lower-order coagulated particles cannot be ascertained, even when the particle size of the dispersed nanomaterials that were identified is equal to the size of coagulated particles. It must be assumed that it may be impossible to detect the primary particles or lower-order coagulated particles when they are hidden by background particles. The composition or shape of the collected sample must be analyzed if there is fear of the primary particle size dispersing. Generally devices for conducting this kind of analysis are expensive, and a high level of expertise is required to properly handle them. For this reason, it is best to consult an organization which specializes in conducting analysis.

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