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Sizing of Colloidal Nanoparticles by Electrospray and Differential Mobility Analyzer Methods

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The goal of this work was to develop a simple technique for sizing colloidal particles by means of electrospray and aerosol techniques. Size distribution of different types of colloids (oxides, metals, and polymers) such as silica, gold, palladium, and polystyrene latex particles, with different nominal sizes below 100 nm was determined online. Nanometer-sized particles were dispersed into the gas phase as an aerosol via electrosprays operating in the cone-jet mode of a colloidal solution followed by a charge reduction of the sprayed droplets to unity and subsequent evaporation of the solvent. The size distribution of the generated aerosol particles was then determined by a differential mobility analyzer combined with a condensation nucleus/particle counter. For comparison, particle sizes were determined by electron microscopy (EM) using the samples which were obtained by (i) naturally dried sols and (ii) on-line deposited on a substrate during electrospraying. The proposed technique is capable of detecting the degree of dispersity of all colloid samples, and the measured values were comparable to results obtained by EM and dynamic light scattering. The results clearly show that the method described here constitutes a convenient, reliable, and rapid tool for the size determination of colloidal nanoparticles.

1. Introduction

The extensive applications of nanoparticles ranging in size from about 1 nm to as large as 100 nm require high-resolution sizing and classification techniques. It is well-known that a rich variety of liquid-phase methods, via chemical approaches such as microemulsion, sol–gel, reverse micelles, etc., are available for producing colloidal nanoparticles. They are also frequently used in studies related to materials science, chemistry, and biology, including macromolecules, sols, nanocrystallites, dendrimers, polymer latexes, and proteins or living cells. Complete knowledge of nanoparticle size and their dispersity is highly desirable, since many of the properties associated with nanosized particles are strongly size dependent.

To analyze the size of colloidal nanoparticles, microscopy techniques such as transmission or scanning electron microscopy (TEM/SEM), scanning near-field optical microscopy,¹ scanning probe microscopy, and atomic force microscopy have been used conventionally.² In these methods, good sampling techniques and skilled operation as well as time-consuming procedures are required. Schmid and Chi³ reported that for a smaller order, the imaging or sizing of metallic Au clusters by high-resolution transmission electron microscopy is usually accompanied by a coalescence process between the cluster molecules, leading to colloidal particles of a larger size in the time order of seconds.

It is important to characterize the size of isolated colloidal nanoparticles without the particles being imbedded within an oxide layer or substrates. A number

instruments involve the use of various principles that have been developed to measure and classify colloidal particles, such as small-angle X-ray scattering,^{4,5} dynamic light scattering (DLS), which is also known as “quasi-elastic light scattering” and “photon correlation spectroscopy (PCS),”⁶ field-flow fractionation,⁷ and analytical ultracentrifugation.⁸ However, the current situation remains particularly challenging and a great need continues to exist for the development of new types of reliable online-sizing techniques with high resolution but which involve sufficient user-friendly facilities.

One of the authors⁹ has proposed an on-line technique for measuring the size distribution of colloidal particles. The procedure involves (i) transferring the colloidal particles from the liquid into gas the phase (as an aerosol) using electrospray and (ii) particle sizing in the gas phase using an inertial impactor or a differential mobility analyzer (DMA). The need to use two instruments in series follows from the fact that the charge on the particles is high and unknown. Very large particle losses in the flow lines between the electrospray and the detector lead therefore to considerable deformation of the size distribution. The capabilities of this technique have been assessed by analyzing colloids of known sizes with standard polystyrene latex (PSL) spheres having nominal diam-

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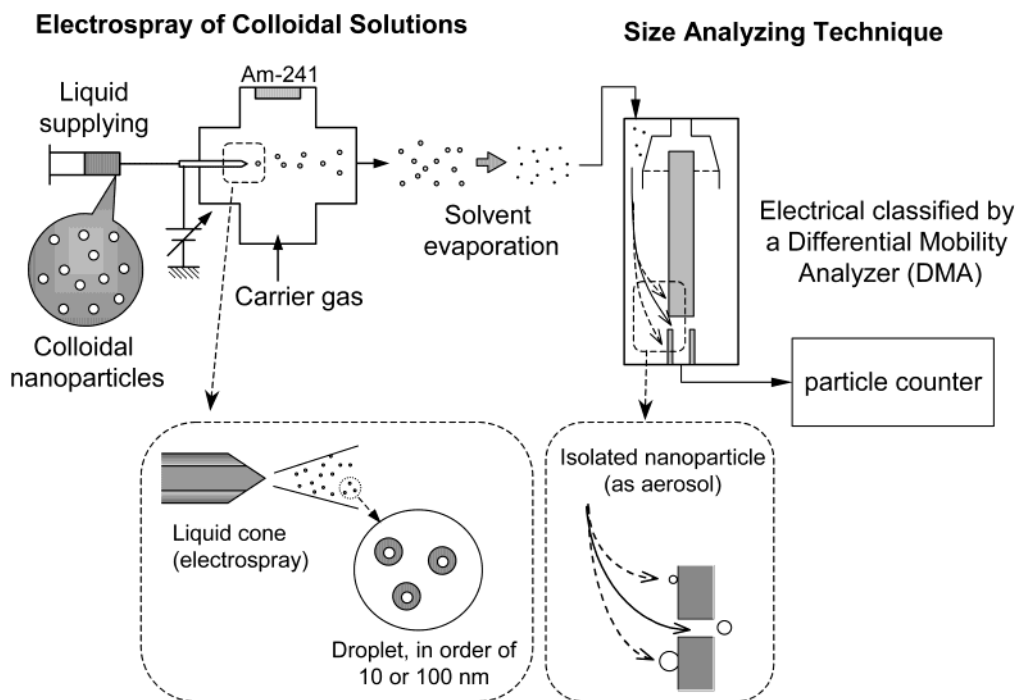


Figure 1. Schematic of the electrospray of colloidal solutions and an online sizing using aerosol techniques.

eters ranging from 74 to 21 nm. However the original study did not provide comparative data relative to other methods, e.g., microscopic analysis. In addition, a need still exists for a measurement method that can be applied to the analysis colloids with "unknown" sizes as well as for smaller particles.

The electrospray technique is one of the few known schemes which is capable of atomizing a liquid into ultrafine droplets. In this method, a meniscus of a conducting solution supported at the end of a capillary tube becomes conical when charged to a voltage of several kilovolts with respect to a counter electrode. Droplets are then generated by the continuous breakup of a steady jet which is naturally formed at the apex of this cone (Taylor cone). The full structure is often referred to as a cone-jet.¹⁰ Electrospray can transfer colloidal nanoparticles from the liquid to the gas phase where the generated droplets are sufficiently small (down to tens of nanometers)¹¹ to capture one particle in one droplet (Figure 1). In the case of other atomization techniques with larger droplets, it is, in practice, difficult to obtain a condition suitable for sizing,¹² which is extremely important in this technique. For example, if the most commonly used atomization techniques, i.e., ultrasonic nebulizers or twin-fluid types that generate droplets in the range of several to tens of micrometers, are used to generate the droplets as low as 0.0008% (in volume), the initial colloidal solution must be satisfied in order to obtain particles 100 nm in diameter from typical initial droplets of 5 μm . In practice, these low solution concentrations lead to difficulties in maintaining a high purity of the colloid. Moreover, a nonvolatile impurity can influence the size of the dried particles as well as the size resolution, in the case of a large droplet.

In the present study, electrospray was used for transferring the colloidal particles to the gas phase followed by sizing the on-the-flight nanoparticles by using a DMA

and a condensation particles counter (also referred to as a condensation nucleus counter, CNC). In this procedure the degree of contamination can be reduced compared to other sizing techniques. As test colloids, we used polystyrene latex, commercial silica, and gold and palladium sols with different nominal diameters ranging below 100 nm in size. Prior to measurement of the particle size distributions, the regime at which the liquid cone and the spray operates was distinguished and controlled. Conditions wherein one particle is captured per droplet were confirmed by controlling the initial sol concentration and the size of sprayed droplet.

2. Experimental Section

As shown in Figure 2, the system used for the online-sizing measurement, which was similar to that reported in our previous study,¹³ consisted of (i) an electrospray source, (ii) a neutralizer, and (iii) a size-analysis section, including a differential mobility analyzer (DMA, TSI model 3071 or 3085) and a particle counter (a condensation particle/nucleus counter, TSI model CNC 3025) operated under atmospheric pressure. The purpose of the DMA is to extract particles that fall within a narrow range of electrical mobility from a steady stream of charged particles suspended in a gas. The narrow range of electrical mobilities in the aerosol that is classified by the DMA directly translates to a narrow range of particle size. This feature has been widely exploited in aerosol research involving particles and ions ranging from around 1 μm down to the subnanometer range.^{11,14}

It is also known that the droplets generated in an electrospray are always highly charged. Hence, the large electrical mobility associated with them leads to considerable losses, as a result of deposition onto the walls, which drastically decreases the overall throughput efficiency of the aerosol/particle. In present study, a radioactive bipolar ion source (²⁴¹Am) was used to neutralize the electrosprayed drops. Charge reduction of the sprayed droplets to unity is essential for the sizing method.¹⁵ In an electrical-mobility detection technique (DMA), the aerosol passes through a bipolar ion neutralizer, which generates a high level

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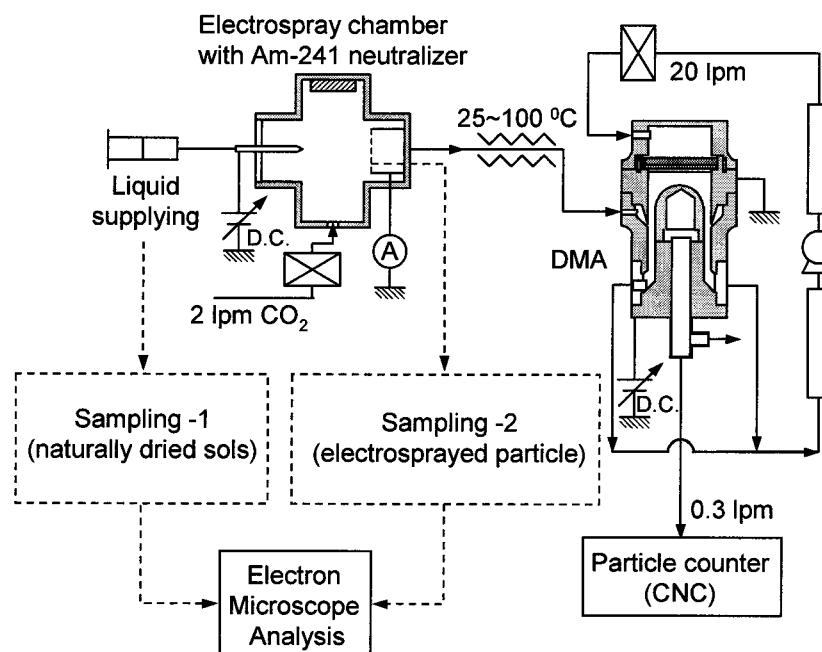


Figure 2. Experimental setup for measuring the size distribution of colloidal particles.

of positive and negative ions. The neutralizer brings the aerosol charge level to a Fuch's equilibrium charge distribution.¹⁴ Nearly all droplets or particles acquire either a single positive, single negative, or zero charge. The particles then enter the differential mobility analyzer and are separated according to their electrical mobility. The mobility distribution obtained is converted to a real size distribution by considering the equilibrium charge distribution.

Several silica sols with different nominal diameters below 100 nm (types ZL, XL, 50, C, XS) fabricated via an ion-exchange process by Nissan Chemical Industries Ltd., Tokyo, were used. Colloidal gold particles with two nominal diameters (referred to as Au-A and Au-B) provided by Professor Takahagi's group, Hiroshima University, were prepared using a procedure reported by Slot and Geuze.¹⁶ Additional gold (Au-T) and palladium (Pd) colloids prepared by a precipitation method (Japanese Patent, 05-155629) were provided by Toda Kogyo Corp., Hiroshima, with the surfactants octadecyltrimethylammonium chloride ($C_{18}H_{37}N-(CH_3)_3Cl$) and poly(vinyl alcohol). A polystyrene latex (PSL) particle with a certified mean diameter of 21 nm and an uncertainty of 1.5 nm (Nanosphere size standards, Duke Scientific Corp., California) was also used in the current study. The certified diameter of this particle size standard was obtained by photon correlation spectroscopy (PCS/DLS). However the manufacturer has noted that the 20–40 nm particle standards are not recommended for aerosol generation, since such suspensions contain a large amount of surfactant which generates a residue when the particles are dried or dispersed as an aerosol.

In this study, colloidal particles were dispersed in a mixture of water/methanol (50:50 vol %) and methanol (water/methanol ratio 0.01:99.9 vol %) in a few cases. Particularly for the colloids with a small size (below 40 nm), to increase the electrical conductivity of the solution in the order of 0.01–0.1 S/m, ammonium acetate at a concentration of between 0.2 and 20 mM was added. The mixture ratio 50:50 of water/methanol¹⁷ and the addition of ammonium acetate¹⁸ have been widely used in electrospray studies. The electrical conductivity of a solution was measured by means of a conductivity meter (Toko Chemical Inc., TX-90) at 25 °C.

It is well-known that high conductivities and a low flow rate of a spray solution allow the generation of small droplets with diameter of a few tens or hundreds of nanometer. Scaling laws can be used to estimate the size of the droplets generated in the

cone-jet mode. Rossel-Llompart and Fernández de la Mora¹⁹ found that droplets are formed mainly in a single size, whose initial diameter, D_d , scales with the parameters described in eq 1. Equations can be given for the case of a polar liquid such as methanol and water with electrical permittivity $\epsilon > 6$ and electrical conductivity K typically larger than 10^{-5} S/m²⁰

$$D_d = G(Q\epsilon_0/K)^{1/3} \quad (1)$$

where Q is the flow rate through the jet (from the Taylor cone) and ϵ_0 is the electrical permittivity of a vacuum. Available data on G were compiled in the literature.^{13,21} G mainly is dependent on ϵ but is also influenced by the viscosity variable.^{19,22}

The proper initial concentration, at which one electrosprayed droplet captures one colloidal particle, can be predicted by estimating the droplet size using eq 1, e.g., by controlling the liquid flow rate Q and controlling the electrical conductivities K of the spraying liquid. To use a colloidal solution which is sufficiently dilute to lead no more than one particle per droplet, the colloidal particle concentration of the starting solution C_s (particles/solution in volume fraction) must be

$$C_s < (D_p^3)/(D_d^3) \quad (2)$$

or

$$C_s < D_p^3/[G^3(Q\epsilon_0/K)] \quad (3)$$

where D_p is the diameter of colloidal particle. If the densities of the colloidal particles and that of the solvent are known values, the initial concentration of the solution in terms of weight fraction can be calculated from that in the volume fraction.

For example, in the case of silica type C with $K = 0.02$ S/m (when 20 mM ammonium acetate was added) and $Q = 0.018$ mL/h, the scaling law predicted the generation of initial droplet diameters in the order of 378 nm. As depicted later in Figure 3e, silica C has an average diameter of 18.5 nm (measured by microscopy). It can be predicted that one would need to prepare

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a C solution of concentration below 0.012 or 0.022 wt % in order to capture one particle in one droplet.

The liquid was sprayed inside a six-way cross stainless steel chamber (Figure 2). Two of the opposing sides were used for supplying the spraying liquid and sampling the generated aerosols. A positive dc high voltage source was connected to the stainless steel capillary having inner/outer diameters of 0.1/0.3 mm. The capillary tip was tapered conically down to nearly zero thickness. The liquid was supplied to the capillary through a high-resolution syringe pump (model PHD 2000, Harvard Apparatus, Holliston). A stainless steel tube with an inner diameter of 5 mm was used to sample the aerosol. Alternatively, to obtain particles sampled after electrospraying for microscopy measurement, a 150-mesh brass grid or a brass plate was placed at the tip of another 5 mm tube (Sampling-2/Figure 2). Several holes were made along the side of the tube for the aerosol to flow through. This sampling tube was grounded through an electrometer (model 6512, Keithley, Cleveland) in order to measure the electric current delivered by the droplets that were deposited on it. This allowed the monitoring of the stability of the electrospray. The spray capillary electrode and sampling tube were set horizontally to facilitate the connection of the spray chamber to a DMA-CNC system. CO₂ was used as a carrier gas because of its relatively high electrical breakdown threshold compared with that of air or N₂. The influence of ambient temperature on the aerosols (nanoparticles) was also investigated. Following this heated zone, the resulting dry silica or gold particles were sized with a DMA-CNC system. The sheath air in the DMA is set to 20 L/min and the flow ratio of aerosol (CO₂) to sheath air is maintained at 0.1. The size and morphology of the naturally dried sols (before spraying, Sampling-1/Figure 2) and particles sampled during electrospraying were observed using a Hitachi S-5000 field emission scanning electron microscope (FE-SEM) and a field emission transmission electron microscope (FE-TEM, HF-2100, Hitachi Ltd., Tokyo) to verify and support the data obtained from the electrospray-DMA (ES-DMA) system.

3. Results and Discussion

Determination of the Stability Domain of Electrospray. Different spray modes may lead to quite different drop size distributions for a given solution. For each sample, we measured typical curves of the electric current versus the applied voltage of the spraying solutions with different concentrations using the apparatus shown in Figure 2. The applied voltage was first increased gradually and then reduced after the liquid meniscus at the capillary tip passed some spray modes. When the applied voltage increased from a small initial absolute value, the liquid on the capillary tip was changed from a meniscus to a dripping mode and then a pulsating mode. Increasing the voltage further increases the pulsating frequency, until, at a critical voltage, the liquid meniscus forms a stable Taylor cone and the current jumps drastically.¹³ For a given solution concentration C_s , a stable cone-jet may be formed only within a certain domain of flow rates Q and applied voltage V , $Q_{\min}(V) < Q < Q_{\max}(V)$, Q_{\min} and Q_{\max} are the corresponding minimum and maximum flow rates.^{10,13,23} This stable domain is affected by C_s and electrical conductivity K of the spraying solutions. It is clear that before measuring the particle size distributions, it is necessary to determine and control the regime at which the liquid cone and the spray operate. Since it has been previously established that lower flow rates of spray liquids generate smaller and more narrowly dispersed electrospray droplets,¹⁹ an attempt was made in this study to maintain Q near the minimum value Q_{\min} . At a certain applied voltage, $V(Q)$, we found that the cone was most easily controlled near Q_{\min} , where the fluctuation of the current is also smallest.

Table 1. Average Particle Diameter (D_p , nm) and Geometrical Standard Deviation (GSD) of Naturally Dried Colloids Measured by Electron Microscopy (EM) and Those Obtained by the Electrospray-DMA (ES-DMA) and a Commercial Dynamic Light Scattering (DLS) Technique^a

sample	D_p (GSD) EM	D_p (GSD) ES-DMA	D_p DLS
PSL	21.0 ^e	24.0 (1.36)	21.0 ^e
ZL	109.2 (1.16)	111.1 (1.15)	136.6
XL	57.6 (1.16)	71.6 (1.14)	74.0
50	29.1 (1.10)	32.6 (1.09)	57.0
C	18.5 (1.25)	19.5 (1.30)	N/A
XS	^f	13.0 (1.17)	N/A
Au-A	7.1 (1.14)	11.5 (1.46)	N/A
Au-B	14.9 (1.10)	19.0 (1.19)	N/A
		17.9 (1.24) ^b	
		14.6 (1.32) ^c	
Au-T	10.9 (1.45)	10.3 (1.16) ^c	N/A
		14.2 (1.26) ^d	
Pd	4.3 (1.51)	9.5 (1.17) ^c	N/A
		8.2 (1.16) ^{b,c}	

^a All ES-DMA experiments were run using a mixture of water-methanol as the solvent at a temperature of 25 °C except for the following: ^b for the run at 100 °C; ^c for the use of methanol (99.9 vol %); ^d for the use of water (the original/raw solution). PSL particle was measured using DLS method (by the manufacturer Duke Scientific Corp.). ^e The DLS measurement of all samples (except ZL, XL, and 50) have no good accurate mean diameter, i.e., no good repeatability (N/A). ^f Below 10 nm.

Photographs and Size Distribution of Naturally Dried Colloids. Size distributions of raw colloidal nanoparticles were obtained by naturally drying the samples prior to SEM/TEM analysis. Figure 3 shows photographs of the naturally dried colloidal particles of silica (Figure 3a–e), gold (Figure 3f–h), and palladium (Figure 3i). More than 600 particles were counted to obtain a size distribution. From these results, the average diameters (number based) of the raw colloidal particles were found to be in the range from 109.2 nm for silica ZL to 4.3 nm for palladium (Pd) as shown in Table 1. Unfortunately, the XS silica sol was not easily analyzed since its naturally dried particles have a sintering-like morphology, as shown in Figure 3e. From their TEM photographs, it is clear that XS is constructed from particles having a size below 10 nm. It is also clear that gold samples Au-A and Au-B have a relatively high monodispersity; i.e., geometrical standard deviations are in the order of 1.1.

TEM observation of the palladium samples (Figure 3i) demonstrates that the Pd particles are insulated from each other by some spaces (white area), which suggests that the particles are encapsulated by a large amount of the surfactants (octadecyltrimethylammonium chloride and poly(vinyl alcohol)). As discussed later, the surfactants generate a residue surrounding the particles during solvent evaporation when the particles are dried (Figure 3i) or dispersed as an aerosol (Figure 7e,f).

Particle Size Distributions of Electrosprayed Colloids. The particle size distributions of the colloidal particles were measured using the ES-DMA system. In each case, the ambient was maintained at a temperature of 25 °C and the liquid flow rate Q was near or at the minimum value Q_{\min} . The influence of initial concentration of the spraying solution on final particle size distribution was investigated as shown in Figure 4. Using an XL silica colloid, four solutions with different concentrations (C_s), 0.33, 0.165, 0.083, and 0.033 wt %, were electrosprayed without added ammonium acetate at room temperature. From the size distributions, it is clear that $C_s = 0.33$ and 0.165 wt % solutions generated dried agglomerated particles with size peaks around 150 and 130 nm,

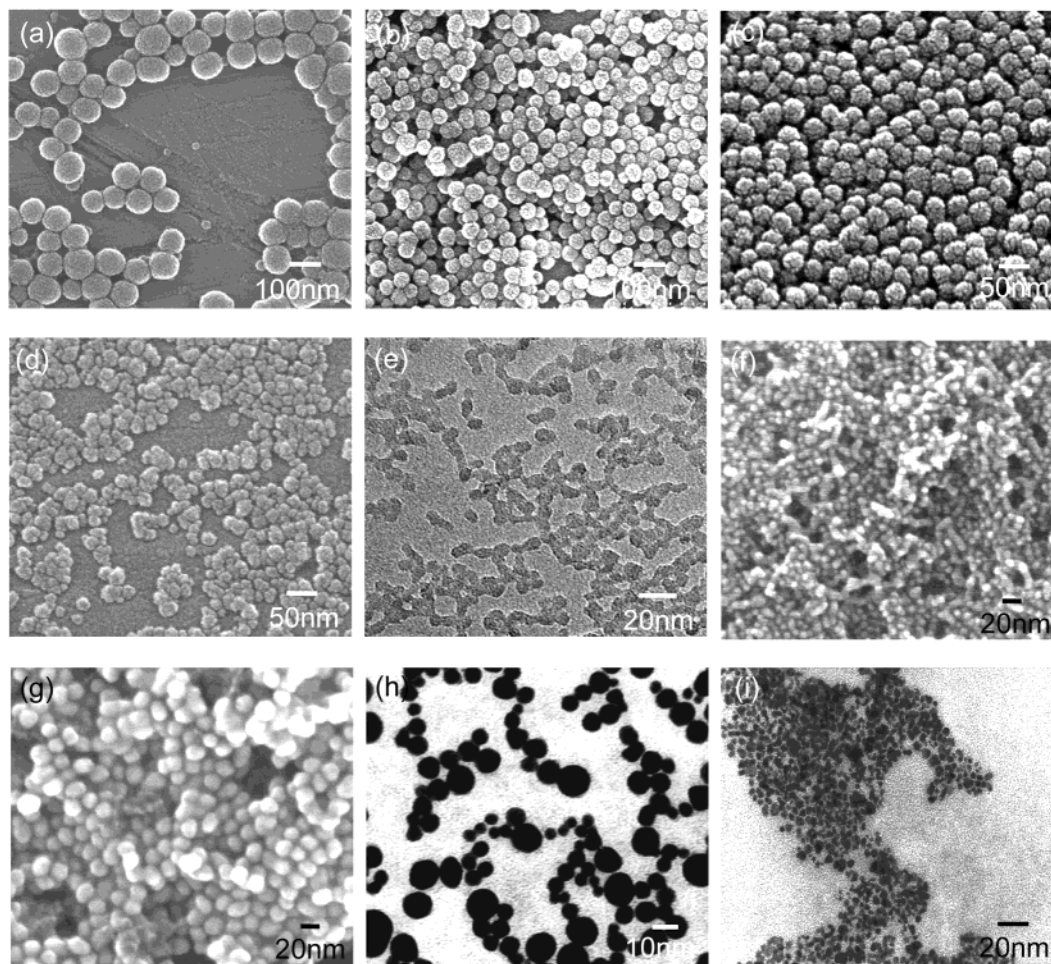


Figure 3. Electron microscope images of naturally dried colloids of silica (a, ZL; b, XL; c, 50; d, C; e, XS), gold (f, Au-A; g, Au-B; h, Au-T), and palladium (i).

respectively. This difference indicates that the initial solution of 0.33 or 0.165 wt % is too high to achieve the condition of one particle per one droplet. Without adding ammonium acetate, decreasing C_s changed the electrical conductivity of the solution substantially from the order of 10^{-3} to 10^{-4} S/m. Meanwhile, another parameter which can also control drop size, i.e., the liquid flow rate, was maintained at a constant value of 0.1 mL/h. Therefore, it is clear that the lower the concentration, the smaller the (agglomerated) particle size. To confirm the generation of an isolated nanoparticle in the gas phase, the XL sol concentration was decreased to 0.083 and 0.033 wt %. The electrosprays of these solutions yielded dried silica particles having sizes of around 72 nm. The size did not become smaller at a lower concentration (0.033 wt %) due to the existence of colloidal particles inside the droplets. By lowering the concentration of the spraying liquid, it is possible to define the condition for achieving one particle per droplet. Electron microscope photographs of the electrosprayed four XL colloids confirm the formation of agglomerated particles and isolated nanoparticles as a function of their initial solution concentrations. In fact, for some colloids prepared in this study, up to five different solution concentrations C_s (10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} wt %) were electrosprayed to confirm the generation of isolated single nanoparticles in the gas phase.

Figure 5 shows the size distributions of particles generated from positive charged electrosprays at room temperature for polystyrene latex (Figure 5a) and various silica samples (Figure 5b–f). By use of the ES-DMA system, the PSL particle (with a certified mean diameter

of 21 nm obtained by the PCS method) was analyzed and the measured average diameter was 24 nm with a geometrical standard deviation of 1.36. It is known that this PSL contains a large amount of surfactant, which will generate a residue when the particles are dispersed as an aerosol. Therefore the size of the PSL aerosol measured by ES-DMA is somewhat larger than that for a hydrosol measured by the PCS method. A discussion on the influence of the surfactant to the measured particle size is also included in the next section.

As also shown in the right row of Table 1, the average diameter and the geometrical standard deviation (GSD), as measured by the ES-DMA system, were in the range from 111 nm for silica ZL to 13 nm for XS. It should be noted that it was difficult to determine the size distribution of XS by electron microscopy. All of the cases (except Figure 5f) show that the measured samples have unimodal particle size distributions. Figure 5f shows the spectrum obtained when the silica C and XS were mixed at the same solution concentration. Both peaks are interpreted as C and XS, respectively. It was very difficult to obtain such a bimodal size distribution result as shown in Figure 5f, probably due to complex interactions involving repulsive forces and van der Waals attractive forces on the surface between two or more colloids having different sizes and properties. None of the runs required any additional dispersion technique or dispersant to decrease the agglomeration of the particles such as ultrasonic and mechanical homogenizer. Although a discrepancy between sizing with ES-DMA and the electron microscope analysis

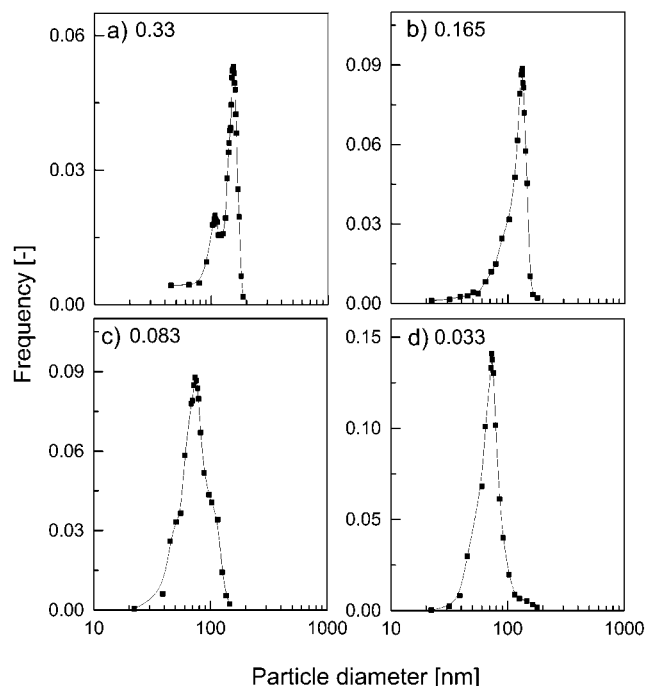


Figure 4. Measured particle size distribution of a silica XL colloid at different initial concentrations of the spraying solution. The numbers indicate the initial concentration of XL in wt %. Spraying flow rate Q : 0.1 mL/h.

(a few percent up to 20%) still exists, we conclude that their measured particle sizes are comparable.

The present results showed that isolated single particles could be generated during the electrospraying of a colloidal solution. Figure 6 indicates that the electron microscope analysis also confirmed the generation of isolated single nanoparticles. In this figure, two of the silica samples and a gold sample (C and Au-B) showed single colloidal particles dispersed on the substrate (TEM grid). Although a sufficient number of electrosprayed particles is not available for a size distribution analysis, the sizes of dispersed particles are in good agreement with those obtained by the ES-DMA system and are shown in Figure 3.

Only a few studies on the discrepancy between size distributions of the same sample obtained with different measurement techniques for colloids having size below 100 nm have been reported.⁵ Lee et al.⁷ reported that with latex particles having diameters ranging from 50 nm to 1 μ m, SEM yielded an average diameter about 20% smaller than those obtained from the PCS and the flow-field fractionation method. For larger particles having a size above 100 nm, Luckham and Ukeje⁶ reported a discrepancy between the average size of the same sample, as obtained with PCS and with TEM. The measured sizes of their narrow distributed polystyrene latex particles were 400 nm for PCS and 380 nm for TEM. Similar to most cases in our study, a shift to smaller diameter from a sizing found by electron microscopy (EM) is likely due to the shrinkage of sample colloidal particles during drying in the high vacuum ambient used in the EM measurement system.⁷

In the case of the silica XS colloid, the naturally dried particles have a sintering-like morphology and were linked with each other. We attempted to analyze small silica (XS, C) and gold (Au-A, Au-B, Au-T) colloids by asking instrument manufacturers to measure their particle size distribution with various techniques based on the transmission of light such as the DLS. However, all samples

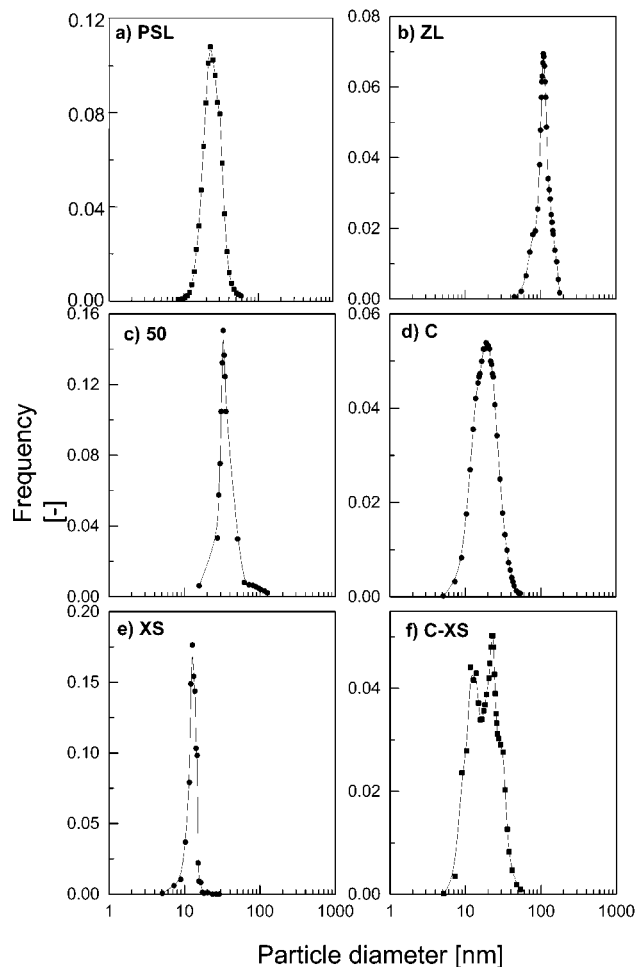


Figure 5. Measured particle size distributions of PSL (a) and various silica colloids, (b) ZL, (c) 50, (d) C, (e) XS, and (f) mixture of C and XS, at ambient temperature of 25 °C. The flow rates were set near the minimum value for Q_{\min} at each run.

have a strong tendency to aggregate, and those techniques resulted in a measured diameter that is quite large (a few hundred nanometers for some samples). Thus, these common techniques are not easily able to detect the size distribution of colloids used in this study, especially those that have a sintering-like morphology. Although some discrepancies still exist between the results measured by the ES-DMA system and those by electron microscope analysis, the present study could easily determine the dispersity of an XS colloid with a measured average diameter of 12.96 nm and GSD of 1.17.

Furthermore, on size measurement using the DLS technique, we have compared five apparatus from different manufacturers. After reviewing the particle sizes obtained from these apparatus, we mainly used the fiber-optics particle analyzer (FPAR-1000) of Photal, Otsuka Electronics Co. Ltd. (Japan). The average particle size (number based) measured by DLS is also shown in Table 1 and all of them show larger values compared with those obtained by EM or ES-DMA. In the DLS, measurements had to be repeated at several runs (e.g., changing the scattering angle) to obtain an accurate mean diameter. In fact, most of our samples have no good accurate mean diameter, i.e., no good repeatability.

Influence of Solvent and Operation Temperature on the Measured Particle Size Distribution. As shown in Table 1, a large discrepancy (21–38%) exists in the measurement of Au-A and Au-B gold colloids, when a water–methanol mixture (50:50) was used as solvent.

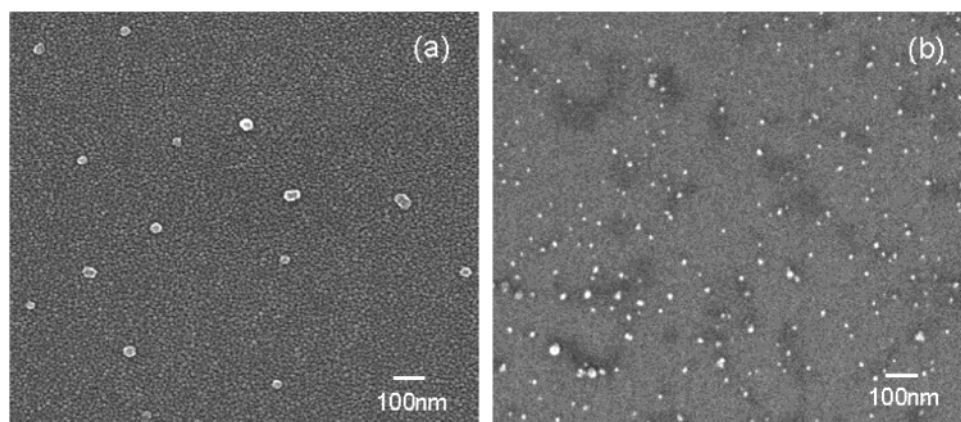


Figure 6. Electron microscope photographs of isolated nanoparticles of silica-C (a) and gold Au-B (b) dispersed on the substrate during their electrospraying at the same condition as those depicted in Figure 5d (silica-C) and Figure 7c (Au-B).

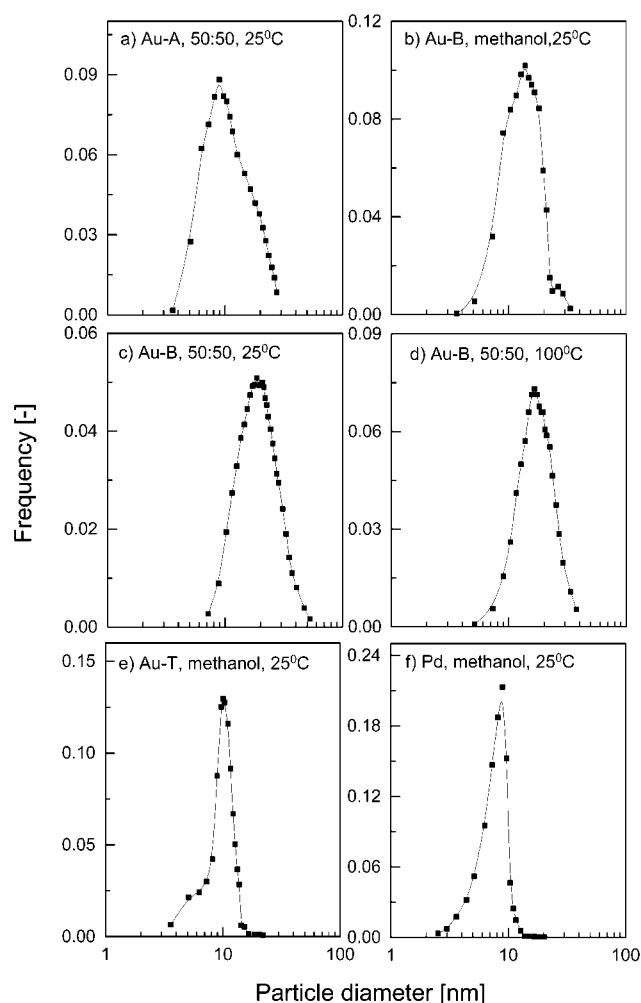


Figure 7. Measured particle size distributions of three samples of gold and a palladium colloid at different conditions. The flow rates were set near the minimum value for Q_{\min} in each run. Experimental conditions (colloid, solvent, temperature) are as follows: (a) Au-A, 50:50 vol % (water–methanol), 25 °C; (b) Au-B, methanol (99.9 vol %), 25 °C; (c) Au-B, 50:50 vol %, 25 °C; (d) Au-B, 50:50 vol %, 100 °C; (e) Au-T, methanol, 25 °C; (f) Pd, methanol, 25 °C.

Table 1 and Figure 7a,c show that the average diameters, as measured by EM and ES-DMA, are 7.1 and 11.5 nm for Au-A and 14.9 and 19.0 nm for Au-B, respectively. These differences might be the result of the existence of an outer layer surrounding the core particles, since metal colloids require a protecting ligand shell or layer to be

stabilized in solution.³ Au-A and Au-B colloids are likely composed of a gold core²⁴ surrounded by a negative ionic double layer. The stability of these gold colloids decreases in the sequence of water, ethanol, chloroform, and benzene solutions.²⁵ It follows, therefore, that the thickness of the outer layer decreases in the above sequence. Using TEM, Huang et al.²⁵ reported that gold nanoparticles (nanodots) were insulated from each other by uniform spaces, which suggest that gold colloidal particles were encapsulated by a layer. We also observed the similar tendency in the case of a TEM image of the palladium (Pd) sample. Among the raw samples with pure water as the solvent, we could form a cone-jet (stable) electrospray in the case of a raw gold colloid Au-T (Toda Kogyo Corp.) without using alcohol or adding ammonium acetate. This is due to the high electrical conductivity of this gold colloid (0.022 S/m). The result, also shown in Table 1, indicates that the technique we introduce (ES-DMA) is not limited to certain solvents such as water/methanol mixtures.

By use of the ES-DMA system, the influences of ambient temperature on the drying process (solvent evaporation) as well as the solvent type on the final particle size were investigated. The temperature was varied between 25 and 100 °C. On the other hand, a mainly methanol-based solvent (methanol–water mixture ratio in a volume of 99.9:0.1) replaced the methanol–water mixture (50:50). Note that initially the raw gold colloids (Au-A and Au-B) were dispersed in pure water. Au-B, which has an average diameter measured by EM of 14.9 nm with the GSD of 1.10, was initially investigated. When the ambient temperature of a path in the ES-DMA system was elevated from 25 to 100 °C, the diameter of Au-B changed from 19.0 nm (GSD, 1.19) to 17.9 nm (GSD, 1.24). This decrease in size was further detected when methanol (99.9 vol %) was substituted for a water–methanol mixture at temperature of 25 °C. The size of the Au-B particles obtained by ES-DMA became 14.6 nm (GSD, 1.32). The discrepancy in the size measured by the ES-DMA and those by the EM is only 2%.

The Pd shows a large discrepancy even though methanol was used as solvent and the operating temperature was elevated to 100 °C. As mentioned previously, this is due to the large amount of surfactants used which form a residue during drying as shown in its TEM images as a white area (Figure 3i). On the other hand, the average diameter of the gold colloid provided by Toda Kogyo Corp.

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(Au-T), as determined by the ES-DMA, is in good agreement with that obtained using EM (10.3 and 10.9 nm). This is probably due to the use of methanol as the solvent in which no "detectable" shell or layer is formed on the surface of the gold particles during the measurement of EM or ES-DMA.

From these results, we conclude that the thickness of a "layer" surrounding a gold particle (Au-A, -B) can be reduced by changing the solvent from water-methanol to methanol or by heating the aerosol. In the case of a "wet" gold particle, a surface layer about 2 nm in thickness was observed. The bulk structure (chemical composition and substructure) and surface morphology of colloidal particles may also play important roles, although the effects of these parameters are usually neglected in most discussions. The present study shows that the outer layer which is present on gold particles can be partially eliminated by changing the solvent from water or water-methanol to methanol as well as by heating the aerosol path.

4. Conclusions

The potential of the electrospray technique in the sizing of nanosized colloidal particles in the range below 100 nm in diameter has been demonstrated by an on-line size measurement using a differential mobility analyzer system and has been confirmed by the electron microscope (TEM and FE-SEM) images of (i) naturally dried colloids and (ii) samples collected during electrospraying. Electro-

spray is able to finely atomize solutions of colloids to nanometer order-sized droplets and allows each colloidal particle to be captured in a different sprayed droplet, i.e., one droplet in one particle. This study also showed that the outer layer, which is formed on the metal particles, could be partially removed by changing the solvent or elevating the ambient temperature. Moreover, the approach described here offers the potential of the rapid online sizing of nanoparticles in solutions.

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