Latest Technology and Standardization Trends for Liquid-borne Particle Counters

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Abstract

Fine particles contaminating into production facilities have significant influence to the degradation of quality of microstructure products. Liquid-borne particle counters are widely used to count liquid-borne particles in the production processes for microstructure products. For evaluating the performance of these counters, some ISO standards have been established. On the other hand, the process for manufacturing leading-edge semiconductor devices requires the measurement of yet smaller particles. Based on research on our company’s development situation, this paper describes the latest trends in small particle detection. It also describes a newly proposed method for evaluating reliability in small particle size measurement not covered by ISO standards.

1. Overview

The µm-scale or nm-scale micro-fabrication technique is used for manufacturing semiconductor devices and liquid-crystal displays. Their quality and yields are significantly influenced by small particles contaminating into their production processes. The International Technology Roadmap of Semiconductors (ITRS), aimed at internationally sharing production technology for leading-edge semiconductor devices, specifies that the controlled contamination particle size should be 20 nm or less in 2011 and beyond.[1] On the other hand, new techniques such as “More than Moore”[1] techniques for achieving the necessary performance of semiconductor devices without increasing their level of integration regarding their structural elements are being implemented for mass production, expanding the types of processes and materials that should be used under contamination particle control. In addition, quality control similar to that of semiconductor materials is required for producing nanomaterials, which are expected to see increased use in the future. As a result, there is a need for the development of measurement technology for smaller particles in many more fields.

Light scattering phenomena are particularly useful for detecting small particles. Light scattering liquid-borne particle counters (LPCs) are widely used for measuring the number concentration of suspended particles. Based on the results of our company’s development efforts, the following describes the principles and configuration of the latest LPCs, the situation and issues regarding the standardization of its performance evaluation technique, and the solutions to these issues.

2. Principles and configuration of LPCs

2.1 Light scattering phenomena

ISO 21501-2 specifies the performance and testing method for the LPC.[2, 3] The ISO standard and JIS standard[4] define LPCs as devices that counts suspending particles by using light-scattering phenomena. G. Mie conducted a strict theoretical analysis of light scattering caused by particles as a propagation of light, which is an electromagnetic wave, occurring at the boundary of media with different dielectric constants. Since then, many studies have been carried out on the numerical and applied solutions for light scattering of particles.[3] Mie's theoretical formulas determine the spatial distribution of particle-scattered light intensities. Parameters used in the formulas are: the intensity and wavelength of irradiated light; the particle size (represented by the size of sphere); the refractive indexes of particles and their surrounding media; and the direction of scattered light (relative to the surface consisting of an irradiated light axis and an electric-field vibration plane of irradiated light).

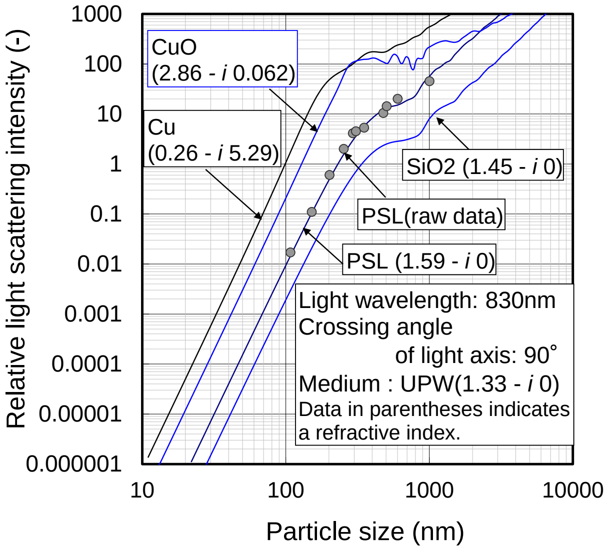


Fig.1 Light-scattering characteristics of particles, derived from Mie's light-scattering theory.

Figure 1 shows the light scattering characteristics, derived from Mie's scattered light theory, of polystyrene latex (PSL), Cu, CuO, and SiO_2 as spheres in pure water. Note that refraction index (N) is typically expressed as $N = n - ik$ (where i is a complex number). In some cases, N is referred to as a complex refraction index, the real part (n) as a refraction index, and the imaginary part (k) as an extinction coefficient. In this paper, the values including the imaginary part are referred to as refractive indexes unless otherwise noted. As the figure shows, the measured values and theoretical values for PSL particles with known sizes and refractive indexes match well, demonstrating the validity of Mie's theory. Cu and other metal particles influence the scattering characteristics of light because their imaginary part has a great value. If they are micro-particles, they tend to cause greater scattered-light intensity than non-light-absorbing particles such as PSL. In addition, the refractive index, which includes an imaginary part, varies significantly depending on the wavelength. Thus, if such particles are measured, the difference of the light source wavelength in an LPC could produce a difference between measurements results.

The light scattering characteristics of particles can be divided into the following three types according to the correlation between the particle size and wavelength.

(1) When the particle size is much smaller than the irradiated light wavelength

The particle-scattered light intensity is not direction-dependent. Thus, the isotropic intensity distribution spreads on the plane at a fixed angle to the polarization direction of irradiated light. Rayleigh's theoretical formula,[5] which can be understood as being approximate to Mie's theoretical formula, is applicable to the characteristics of this type so that the scattered-light intensity is proportional to the sixth power of the particle size and inversely proportional to the fourth power of the wavelength. Thus, to decrease the measurable size of particles with the characteristics of this type requires significantly improving the detection sensitivity.

(2) When the particle size is close to the irradiated-light wavelength

The outstanding features of Mie's light scattering theory are clear in this case. Forward scattering is dominant, and the angle distribution of scattered light intensity is complicated. As a result, a monotonic increase in the scattered-light intensity associated with the particle size might be prevented depending on the scattered light condensing angle.

(3) When the particle size is much larger than the irradiated light wavelength

The diffraction of irradiated light due to particles is dominant. The scattered light intensity is roughly proportional to the square of the particle size.

2.2 Principles and configuration of the LPC

2.2.1 Generic LPCs

Figure 2 shows the configuration of the particle detection part (model KS-42B by Rion) of an LPC that can measure particle sizes down to 200 nm. Laser light emitted from the semiconductor laser increases the light energy density in the particle sensing region. Thus, the emitted laser light is changed in sheet-like by the cylindrical lens in the direction of particle passage. The flow channel in the flow cell composed of transparent materials such as quartz or sapphire serves as the particle detection part. If the sample is water, laser light enters the flow channel at an angle of about 35º. The light receiving lens in which the axis is perpendicular to the flow channel collects laser light, scattered by particles in the sample, onto the photo-detector. The axis of the light receiving system is located ahead of irradiated light, enabling the efficient condensation of forward-scattered light. Laser

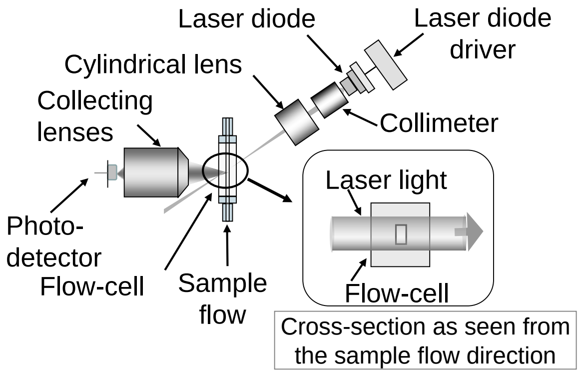


Fig. 2 Particle detection part of liquid-borne particle counter for 200nm.

light obliquely enters the flow cell, which is entirely composed by transparent materials. Thus, stray light generated at the intersection between irradiated light and the flow cell wall surface can easily be separated from particle-scattered light through a slit near the image location immediately above the light-receiving element. As a result, all particles in the flow channel can be measured by radiating laser light that is wider than the flow channel width. This LPC is already a *de facto* standard for counting submerged particles because it can perform quantitatively reliable measurement.

2.2.2 Measurement of particles smaller than 100 nm

Particles with sizes up to 100 nm have the characteristics described in Section 2.1 (1). As the particle size decreases, the sensing signal drastically becomes smaller. Since there are limits to both an increase in the output of a practical laser light source and a decrease in its wavelength, decreasing the sectional area of irradiated light is necessary for increasing the light energy density in the particle sensing region. A reduction in the sectional area of the flow channel is restricted due to the exchangeability of fluid resistances or samples. Thus, a method, called the "partial detection technique," in which laser light irradiates only part of the sample flow, is used.

The full exposure (total counting) technique described in Section 2.2.1 irradiates the entire cross section of the flow channel using light of almost uniform energy intensity. This makes it possible to properly determine the particle size from the scattered light intensity regardless of the particle passage position. The partial detection technique, however, causes the distribution of the energy intensity of irradiated light in the particle sensing region to take the form of a gauss distribution so that the energy intensity of irradiated light differs depending on the particle passage position. That is, the size of detectable particles depends on that of the sensing region, and the probability of detection decreases with smaller particles.

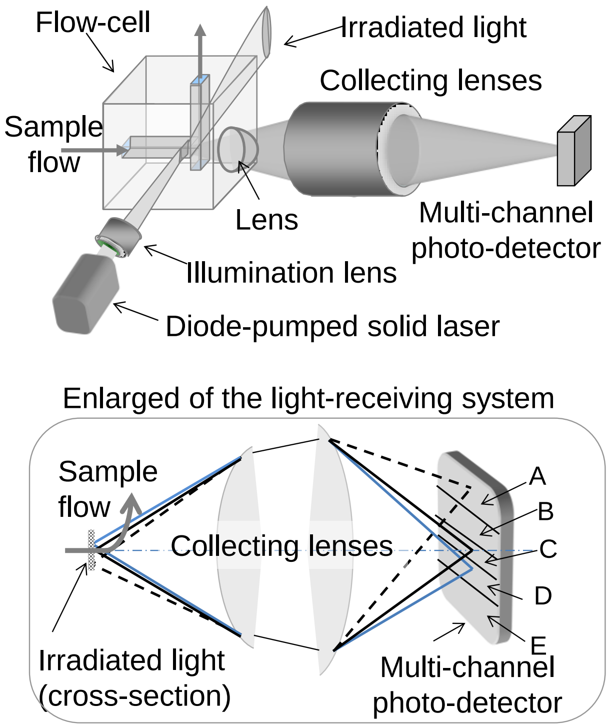


Fig.3 Particle detection system of liquid-borne

One reason that the counting efficiency achieved by the partial detection technique is quantitatively insufficient is that the detection characteristics vary depending on the particle size as described above.

Thus, the particle detection part (model KL-30A by Rion) shown in Figure 3 has been developed to decrease the particle size dependency of the counting efficiency.[6] For detecting particles of smaller than 50 nm, the wavelength is shortened by using a light source that is a second-harmonic light of a laser-diode-pumped YVO4 laser (532 nm, output: 500 mW). The L-shaped configuration of the flow cell allows the light receiving system to be positioned opposite to the sample's flow line. As a result, scattered light of a particle collected onto the photo-detector does not draw a trajectory, and the light focusing position is fixed. As the light focusing position corresponds to the particle passage position in irradiated light, the particle sensing region size and detection sensitivity can be made constant by determining the particle passage position with the multi-channel photo-detector shown in the enlarged illustration in Figure 3 and by judging the selection criteria and correcting signal size for each particle-sensing signal. For this example, the observation region for channels B, C, and D is an effective particle sensing region, and the sensitivity of channels B and D is set equivalent to that of channel C by properly adjusting the amplification factor for the photoelectric conversion signal. There is a possibility that when large particles pass through the edge of the flow channel, channels B, C, and D may be irradiated with faint scattered light. Signal detection in channels A and E eliminates misdetection in channels B, C, and D, which is due to large particles passing through irradiated light outside the effective particle sensing region. As a result it can produce constant counting efficiency.

3. LPC performance evaluation

This section shows the basic performance requirements, stipulated by the LPC standards (ISO 21501-2 and JIS B 9925). It also shows the testing problems and newly proposed techniques.

3.1 Threshold settings for particle size ranges

The particle size ranges of the LPC correspond to the equivalent size of light scattering, and thus sharing the calibration particles is necessary. The standards[2, 4] stipulate that they should be nearly spherical particles along with a refractive index of about 1.59 (for Na D lines) and that the number-mean-size should be traceable to international standards (standard uncertainty: 2.5 % or less). Actually, they are limited to PSL particles created by an emulsion polymerization reaction. The pulse height distribution of the sensing signal of the calibration particles is measured to obtain the median value (voltage) of the distribution as the corresponding size of the test particles. Each value of a particle size setting is calculated on the basis of the corresponding size of the calibration test particle, using Mie's scattering theory. A particle size corresponding to the median value for measuring the calibration particle with a size in a particle size setting should be within ± 15% of that size in the particle size setting. The test measurement values include the uncertainty of the number-mean-size for the test particles. They also include errors in the measurement of the pulse-height distribution of

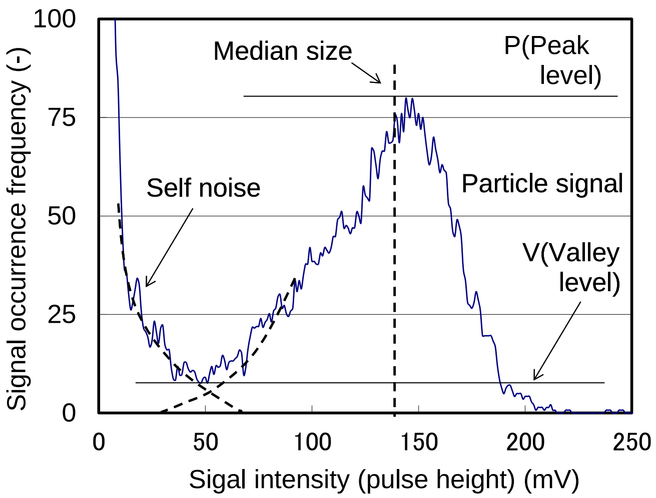


Fig. 4 Pulse height distribution for test particle-sensing signals.

the particle sensing signal. Thus, they should be sufficiently smaller than the required test measurement values.

Figure 4 shows an example pulse-height-distribution of particle detection signal. For particle sizes close to the lowest measurable value, the LPC's self-noise and particle-sensing signals overlap each other. The standards[2, 4] stipulate that the peak of this distribution (P shown in Figure 4) should be two or more times higher than the valley (V shown in Figure 4) for determining the median size from the particle signal distribution. As a result, increasing the CV value of the test particle size (variation coefficient, which is the ratio between the standard deviation and average size) might increase the difficulty in determining the median size. And new calibration particles should be selected because PSL particles with sizes up to 30 nm that can be traceable to international standards have yet to be developed.

3.2 Counting efficiency

The standards[2, 4] is requesting the following items to LPC by making into a standard the microscopy method for counting particles trapped on a membrane filter.

(1) 50 ± 30% when the calibration particles with sizes close to the lowest measurable size are measured with the minimum particle size threshold

(2) 100 ± 30% when the calibration particles 1.5 to 3 times larger than the lowest measurable size are measured with the minimum particle size threshold

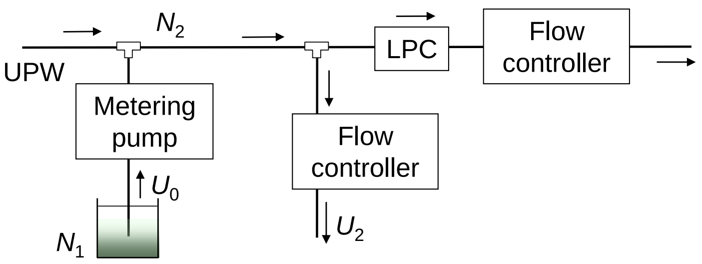
Number concentration standard suspensions, calibrated by a transmission electron microscopic technique, are commercially available. However their particle sizes are over 200 nm. Currently, the particle size for the number concentration approved by public institutions is 5 μm or more. Thus, a total counting type LPC in which performance does not depend on particle size is calibrated using a microscopic technique for particles of about 5 μm. Then, this LPC is used as a reference tool to determine the counting efficiency in comparative testing. However, the reference tool needs to count all test particles with sizes close to the lowest measurable value. Thus, if the lowest measurable size of test particles is 100 nm or less, this reference tool is actually difficult to use.

3.3 Evaluation of counting performance using a quantitative dilution technique

A technique for quantifying the mass concentration and dilution factor for test particles is already standardized.[7] This technique is available to evaluate the counting performance of an LPC for particles smaller than 100 nm. Commercially available PSL particles with a known mass concentration are suspended in pure water. The PSL particles are nearly spherical particles that have a defined specific gravity (1.05 g/cm^3). Most CV values for these particles down to 50 nm are extremely small, not exceeding 3%. This allows these particles to be used as spherical particles that have a median size as a representative value. Therefore, so long as the probability of the particles in which sizes are sufficiently larger than the median size existence is negligible, their mass concentration can be quantitatively converted into a number concentration.

An undiluted solution containing the PSL particles is diluted quantitatively until its concentration reaches the measurable concentration for the LPC. As a result, the number concentration of the PSL particles is quantified using the number concentration and dilution factor for the undiluted solution, making it possible to evaluate the counting performance of the LPC with a known test particle number concentration.

Figure 5 shows the procedure for testing counting performance using the quantitative dilution technique. Test particles with a known number concentration of N_1 are quantitatively injected into pure water at a flow rate of U_0 while the water is supplied at a constant flow rate. The sample flow rate U_1 for the LPC is controlled in the lower course, and the flow rate U_2 is fixed for discharging water to the bypass. The practical limit for the dilution factor should be about 10^6 in view of the accuracy of each measurement device. On the other hand, the mass concentration of an undiluted solution containing commercially available PSL particles is about 1%. Thus, the number concentration of an undiluted solution containing particles of 50 nm is about 1.5 x 10^{14} particles/cm^3. As a result, the undiluted solution is diluted by a factor of 10^5 to 10^6 and entered as the primary diluted liquid into pure water. This primary diluted liquid is made by sampling quantitative volume (V0) and dropped into pure water, which volume is V1, by using a micropipette. The number concentration, N_2, of PSL particles to be introduced into the LPC is determined as shown below. The counting efficiency offered by the LPC



N_2 : Sample number concentration
U_1 : Measured sample flow rate
U_0 : Flow rate of the primary diluting fluid
U_2 : Bypass flow rate
N_1 : 3-10. Number concentration of the primary diluting fluid

Fig. 5 Block diagram of the quantitative dilution test.

can be determined by comparing the LPC count value and N_2 with each other.

$$N_2 = N_1 \frac{U_1}{(U_0 + U_1)} \qquad (1)$$

$$\text{Where,} \quad N_1 = N_0 \frac{V_0}{(V_0 + V_1)} \qquad (2)$$

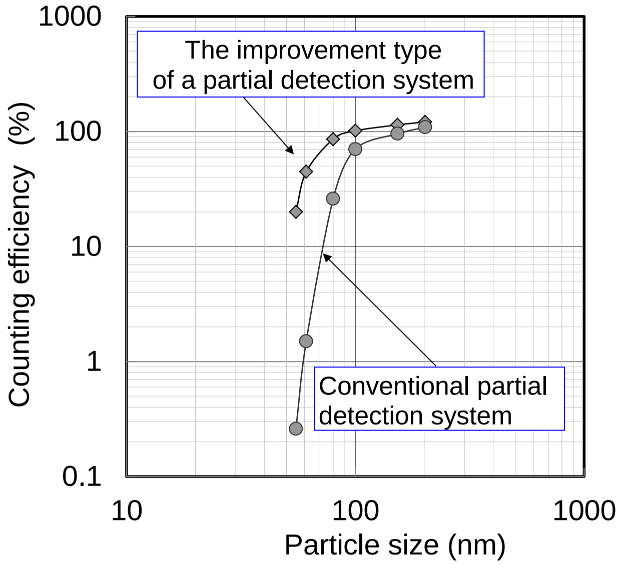


Fig. 6 Evaluation of particle counter performance by a quantitative dilution technique.

Figure 6 shows an example of evaluating the counting performance of an LPC which measurable particle size is 50 nm. This evaluation is based on the number concentration determined by the quantitative dilution technique. The sizes of test particles are plotted along the horizontal axis. The rates between the number of particles which should be counted and the actual counts for particle sizes measured with a minimum particle size threshold are plotted along the vertical axis. The particle counts to be measured are values calculated from the effective sample flow rates (= Introduced sample flow rate x Counting efficiency) presented in the specifications for each LPC. Heretofore, it has been difficult to quantitatively evaluate the counting performance for particle sizes close to the lowest measurable value, but now, this evaluation can be easily performed. The particle size dependency of the counting efficiency shown in Figure 3 can be quantitatively evaluated with ease.

3.4 False counts

The LPC generates false counts even when there are no particles to be counted. False counts are evaluated by measuring a sample with no particles in it. However, creating such a liquid sample is not easy. LPCs can detect and count particles even in highly purified UPW (ultra pure water) containing about 100 particles/L of 50 nm, and the obtained counts might include false counts, which are difficult to evaluate. The standards[2, 4] stipulate that the upper confidence limit on the occurrence rates for false counts should be depicted as 95% in the performance specifications for each LPC. However, these standards do not clarify an actual evaluation technique.

Figure 7 show the results of the 10 minute measurement (effective measurement volume: 20 mL) of

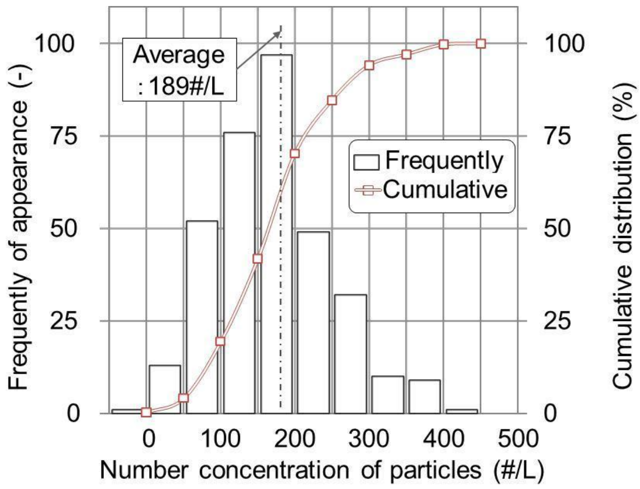


Fig. 7 Measurement of particles in UPW using liquid-borne particle counter for 50 nm.

a number of particles down to 50 nm in UPW. This measurement was repeated consecutively during a period of 72 hours, using an LPC (KL-30A by Rion), which features a sample flow rate of 20 mL/min and a counting efficiency of 10% (effective sample flow rate: 2 mL/min). The number concentrations determined from a particle count for each 10 minute period are plotted along the horizontal axis. The occurrence rates for the particle counts are plotted along the vertical axis. The average of all measurement values is about 189 particles/L, which roughly agrees with the maximum occurrence rate. Since there is neither an uneven temporal distribution of the particle occurrence frequency nor abnormal particle counts by LPC itself, it means that the measurement values are reliable.

The occurrence of false counts is mainly due to reasons such as unstable output of light source, the responses of photo-detectors to foreign high-energy rays (cosmic rays, radial rays, etc.), and quantum noise of the photo-detector itself. When false counts due to light source are detected, such might be increased superposed light noise caused by light source degradation. Or, there might be other phenomena such as unstable output at the time of transition to longitudinal mode. These phenomena consecutively take place in a given period so that the LPC abnormally counts too many particles in a short time. In contrast, false counts due to photo-detector are detected randomly and inconsecutively in most cases.

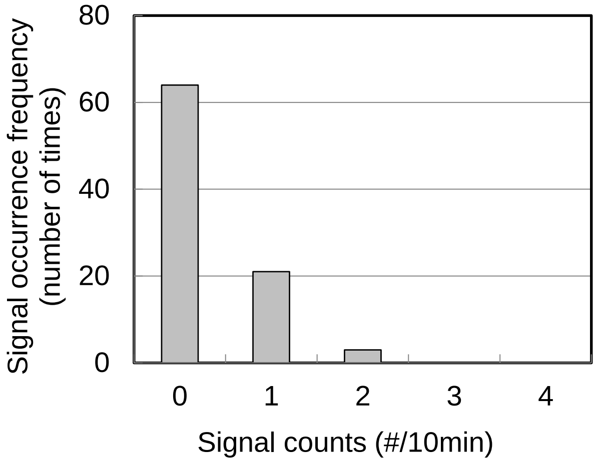


Fig. 8 False count occurrence frequency.

For the measurement example shown in Figure 7, false counts were not consecutively detected during a short period. This is because they were not due to light source. Figure 8 shows the results of the measurement of occurrence rates for false counts due to photo-detector. For measuring these occurrence rates, the light receiving system was covered to protect it from irradiated light, and the sensing threshold for the minimum measurable particle size was used. A 10-minutes measurement was repeated 88 times. The average occurrence rate for false counts was about 0.31 particles/10 minutes. This value corresponds to 15.5 particles/L for the effective sample (2 mL/min) for this LPC. Since 2σ for one side corresponds to about 68 particles/L, the measurement values shown in Figure 7 are those negligibly affected by false counts. Thus, the evaluation of the value of about 100 particles/L using this LPC is considered appropriate as the number of particles in ultra-pure water.

4. Conclusion

Currently, the standards are stipulating that LPC calibration and evaluation should use PSL particles. However, PSL particles do not always provide enough of an advantage as the standard particles for the measurement of particles of smaller than 50 nm, which will be needed in the future. We should study new standard test particles for this purpose. A method[8] of determining the trapping efficiency as the mass of particles has been proposed for testing the performance of liquid filters available for the production of leading-edge semiconductor devices. One of the drawbacks of this method is that its use results in the information of the particle size being lost. Thus, the possibility of using particles that can easily be detected by LPCs is under investigation. The National Institute of Standards and Technology (NIST) issued reports[9, 10] on several sizes of Au colloidal particles. These reports are intended to share the test particles. Figure 9 shows the results of measuring Au and PSL particles in UPW by using the LPC shown in Figure 3. The nominal sizes of particles are plotted along the horizontal axis. The relative light scattering intensities are plotted along the vertical axis. The theoretical curve was matched to the measurement values obtained for 55 nm PSL particles. The refraction index for a wavelength of 532 nm is 1.595 – i0 for PSL particles and 0.467 – i2.41 for Au particles.[11] As this figure shows, the correlation between the actual measurement values for PSL and Au particles agrees well with the theoretical values. For a wavelength of 532 nm, the detection sensitivity for PSL particles of 50 nm is the same as that for Au particles of about 23 nm. This means that the trapping performance

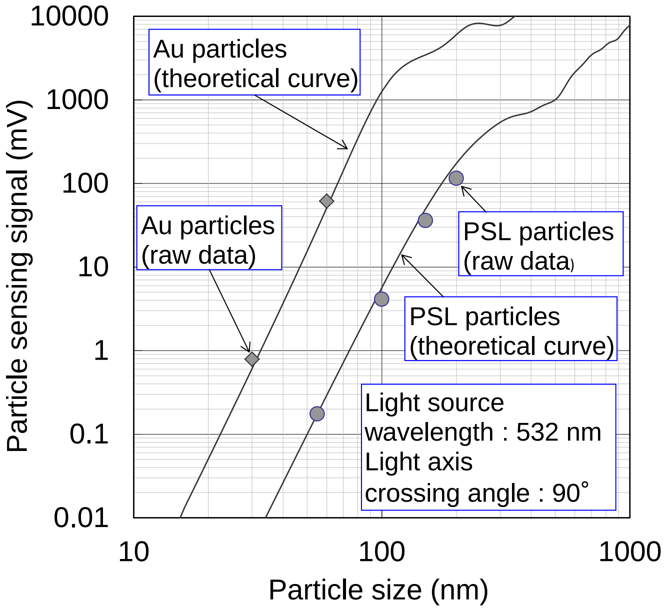


Fig. 9 Light-scattering characteristics of PSL particles and Au colloidal particles

characteristics of the filter for particles of about 20 nm can be evaluated by using the LPC. If public institutions further evaluate particle sizes and refractive indexes, then metal or metal oxide colloidal particles will probably become available as calibration particles.

The control of sub-20-nm particles is necessary for manufacturing leading-edge semiconductor devices. Therefore, we need to develop a new measurement technique. We also need to improve the reliability of measurement values, and thus an evaluation technique that involves quantitative dilution has been proposed. We think that further cooperation among domestic and overseas manufacturers and users as well as public evaluation institutes is vital to sharing not only selection criteria for new standard particles but also evaluation techniques.

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