The Model PLCA-700 Liquid-Particle Counter

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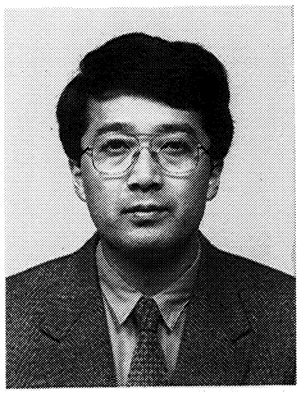
Abstract

With the rapid advances in technology in the manufacturing world, at state-of-the-art production plants for semiconductors and other high-tech products, it has become necessary to control both the size and the concentration of particles in numerous types of chemical solutions. The types of solutions actually used in the production process frequently include acids, strong alkaline substances, and various organic solutions. The physical properties of these substances especially the refractive index, vary greatly, making it difficult to measure the particles in these solutions. Today we are faced with the problem of measuring extremely large volumes of solution that contain a relatively low concentration of particles that need to be checked. The traditional method of filtering the solutions to measure particles has a number of inherent problems that make it inadequate for today's needs. To meet these needs, Horiba has developed and begun to produce the PLCA-700 liquid-particle counters. The PLCA-700 Series measures particles using a laser side-scattering principle. This paper gives an overview of the PLCA-700 liquid-particle counter and discusses the underlying measurement principle, with an introduction to the calibration method of the unit.



1. Introduction

In production plants for super LSIs that exceed an integration level of 16M bits, particles must be strictly controlled. The super deionized water used in such plants requires that the number of particles with a diameter of 0.05 μm be limited strictly to a maximum of 10-20 per cm^3 [1]. Also, in production lines for chemicals, smaller pore diameters on the final filter are being used, from 0.2 μm to 0.1 μm or even 0.05 μm. At present, some kinds of chemicals have less than 10 particles with a diameter of 0.2 μm per cm^3 (see Table 1) [2]. Accordingly, there is a need for particle counters that can measure particles with a diameter of 0.1 μm or less. In addition, the production lines for optical devices, including optical fibers and liquid crystal devices (LCD), require control of particles.

Table 1
Particle concentration in various Chemical solutions. (pcs/mℓ)

	≥0.2μm	≥0.5μm
HCℓ	4.7–10.0	1.2–5.0
HF	0.59–2.0	1–2
HNO_3	3,300–7,800	600–700
H_2O_2	37–107	8–29
H_3PO_4	632–1123	78–221
H_2SO_4	950–1,200	17–860
NH_4OH	390–1,800	64–67

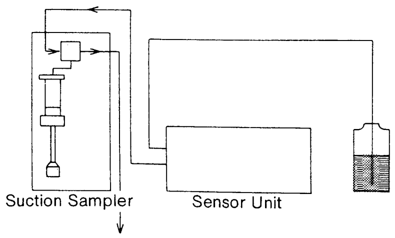
HORIBA manufactures and sells the Model PLCA-520 Liquid-Particle Counter suited for on-site control in factories. Considering the above background, however, we have introduced the new Model PLCA-700 series, with three new models of sensor units added to the line-up. This series has been developed by adding bi-directional communication capability to the conventional counter unit and can be operated from a personal computer. This article introduces the three new sensor units and discusses the configuration, the measuring method, and the calibration method of the Model PLCA-700 series; particular attention is paid to the SNS-20 sensor unit, which has been developed especially for off-line measurements, i.e., batch measurements.

2. OVERVIEW OF THE SYSTEM

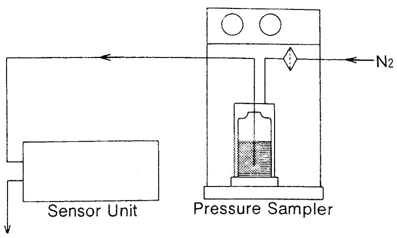
Liquid-particle counters have been used to measure large-diameter particles of approximately 10 μm which exist in injection solutions. In the machine-tool field, they have been used to measure particles of 1 μm in cutting-oil and in lubricants. On the other hand, with today's advances in the semiconductor industry, a liquid-particle counter which can measure particles of 0.1 μm is now required. Under the circumstances, various cells with different structures for particle counters have been devised and put into commercial production. Whatever structures these various cells may have, the measuring method used is either one of two types: (1) the total-measurement type, which measures the entirety of the sample flowing into the cell, or (2) the partial-measurement type. which measures only a portion of the sample flowing into the cell. Those particle counters which are now available for practical measurements of particles of below 0.1 μm often use a cell of the partial-measurement type to eliminate the stray light generated in the cell. The Horiba PLCA series uses this partial-measurement type.

The conventional window material for the cell is either quartz (SiO_2) or sapphire ($A\ell_2O_3$). The liquid-particle counter for the PLCA series uses sapphire.

There are two sampling methods, suction method and pressurizing method. It has been pointed out that the suction method has the drawback of creating air bubbles. However, the generation of air bubbles can be decreased by using a suction method with both a lower differential pressure and a lower flow rate; then the sampling can be carried out easily. Therefore, both this method and the pressurizing method are now in use. See Fig. 1.



(A) Suction method



(B) Pressurizing method

Fig. 1 Sampling method

As the measured particle size has become smaller, the on-line method has been used for on-site measurements along with the suction and pressurizing methods. In particular, when a particle size of below 0.1 μm is measured, a large quantity of the sample is required because both the piping line and the sensor unit are cleaned. Most of the particle counters that are now used in the production site employ the on-line method. The PLCA series includes on-line type counters, allowing the sensor units to be selected in accordance with your on-site needs.

3. CONSIDERATIONS IN DEVELOPMENT

The following three points were considered in the development of this new series of liquid-particle counters:

① The device must maintain resistance to chemical solutions over a long period of time.
② It must be basically safe when operated.
③ Maintenance must be simple.

Considering the need for chemical resistance, sapphire is used for the cell window; a Kalrez type O-ring for the seal; and polytetrafluoroethylene (PTFE) or polytetrafluoroethylene-perfluoro (alkyl vinyl ether)(PFA) for other parts that come into contact with chemical solutions (i.e., wettable parts). In order to ensure simple maintenance, the counter was designed so that (1) the laser head could be replaced on-site and (2) the cell could be cleaned with minimum disassembly.

Table 2 shows the specifications of the sensor units for the PLCA-700 series. The Model SNS-20 is designed for measuring particle sizes of 0.2 μm by the off-line method; the Model SNS-21 for measuring particle sizes of 0.2 μm by the on-line method; and the Model SNS-22 for measuring 0.1 μm by the on-line method. Fig. 2 is an external view of the PLCA-700 series.

Table 2
Specification of the sensor units for the PLCA-700 series

Item	SNS-20	SNS-21	SNS-22
Measurable range	0.2-10μm	0.2-5μm	0.1-1μm
Sample volume	5mℓ/min	10mℓ/min	0.5mℓ/min
Flow rate of sample	20mℓ/min	100mℓ/min	100mℓ/min
Max. concentration	1×10^3/mℓ	1×10^3/mℓ	1×10^4/mℓ
Resolution of particle size	Single peak (available)	Single peak (available)	Flat (not available)
Beam position detector	2 pcs	2 pcs	2 pcs
Measuring principle	Laser scattering method using semiconductor laser		
Sample condition	Transparent liquid containing no air bubbles, with viscosity of 30×10^{-3} Pa·s maximum		
Sample pressure	Less than 3 kg/cm^2		
Light source	Semiconductor laser of approx. 800 nm		
Light detector	PIN photo-diode		

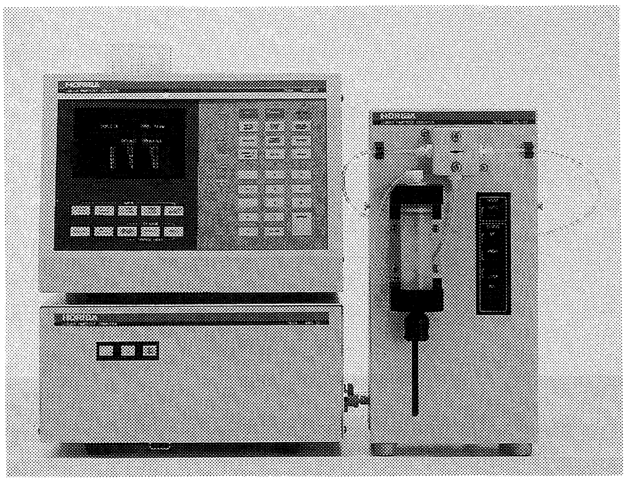


Fig. 2 The PLCA-700 liquid-particle counter

4. MEASURING PRINCIPLE OF MODEL SNS-20 SENSOR UNIT

4.1 Overview of Particle Detection System

The measuring principle of the PLCA series is the lateral laser-beam scattering method (90°). Fig. 3 shows the measuring principle of the Model PLCA-700 with the Model SNS-20 sensor unit.

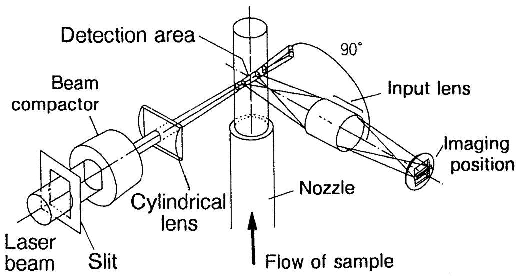


Fig. 3 The Model SNS-20 SENSOR UNIT: principle of measurement

Laser beams with a wavelength of approximately 800 nm, which have been emitted from the semiconductor laser element, are aligned in parallel as they pass through a collimator lens and are then projected from the laser head. The optical intensity of the laser beams is now distributed into a gauss-like state. Next, both ends of the beams are cut off by the slit. The laser beams then pass through the beam compactor, which makes the beam diameter smaller; then they are condensed by the cylindrical lens onto the detection area, located on the upper end of the sample jet nozzle in the measurement cell. The intensity of the laser beams is approximately 30 mW in the stage before going into the slit.

The beams scattered by particles in the sample located in the detection area are condensed by the wide-angle input lens and then imaged on the silicon light detector. The pulse-like optical electric current generated in the light detector is converted to voltage signals by the preamplifier. After passing through the band-pass filter, it is counted as a pulse number in accordance with the particle size by the counter circuit in which the threshold voltage has been determined.

4.2 Incident Optical System

Fig. 5 shows the top and front views of the incident optical system. Since the particle counter requires high resolution of particle size, some method must be used to eliminate the weak portion of the laser beams, i.e., *skirt-cutting*. The Model SNS-20 uses a relay lens system to do this. The slit position is determined so that the slit is imaged at the center of the detection area. If the relay lens system is an ideal imaging system, ideal *skirt-cutting* is possible at the center of the detection area. Fig. 4 shows the distribution of light intensity at the center of the detection area.

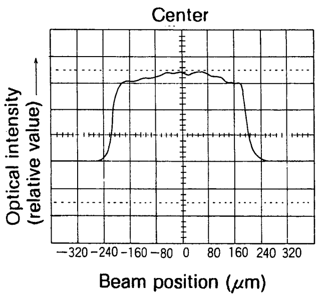


Fig. 4 The Model SNS-20 SENSOR UNIT: strength of the beam in the horizontal direction in the center of the detection area

The light condensation by the cylindrical lens is necessary to decrease the volume of the detection area. If this volume is too large, more than one particle can occur simultaneously in the detected portion when the particle concentration becomes higher. As a result, if this happens, multiple particles will then be counted as a single particle, showing a lower value than the actual concentration.

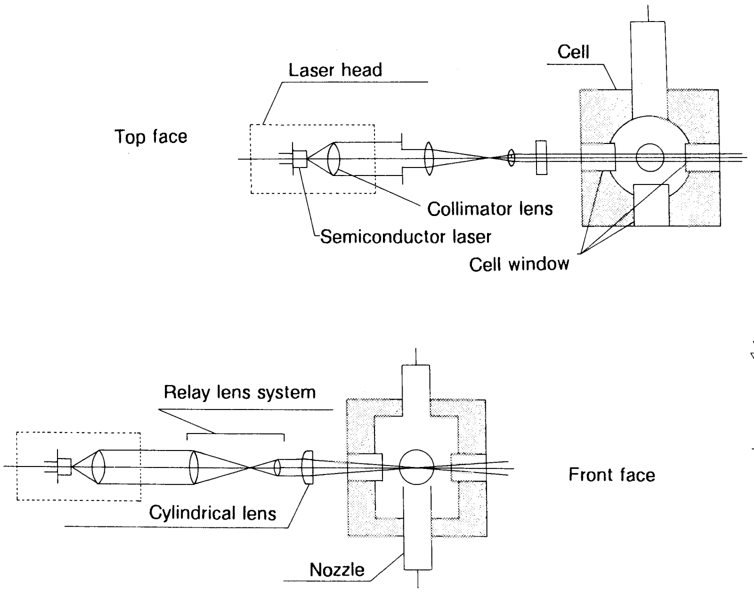


Fig. 5 The Model SNS-20 SENSOR UNIT: incident optical system

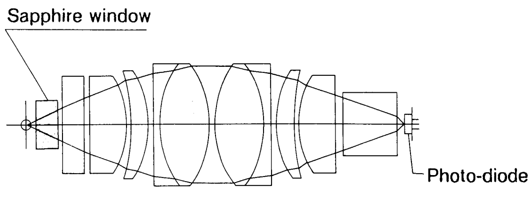


Fig. 6 Arrangement of the input window and the light-gathering optical system

4.3 Input Lens System

Fig. 6 shows the general configuration of the input lens system. The input angle has a half angle of is 30°. Fig. 7 shows that, based on the Mie scattering theory, the graph of particle size vs. pulse-height characteristics for the standard particle (polystylene latex particle, n = 1.59) shows good matching with the experimentally measured values.

4.4 Flow Sheet and Distribution of Flow Rate

Fig. 9 shows the arrangement of the sample flow and the detection area. In the cleaning mode, the sample flows through both the nozzle and the cleaning line, which also serves as an optical trap to prevent the background scattered light from reflecting on the cell wall. In the measurement mode, the sample flows only through the nozzle, because the solenoid valve (SV-3) is closed.

The sample which has entered the nozzle passes through the cylindrical duct that has sufficient length to form a laminar flow. As shown in Fig. 8, it is then jetted to the interior of the cell while maintaining the $Y = 1/X^2$ type speed-distribution. At the outlet on the nozzle, this speed distribution is maintained quite well. In addition, a coneshaped portion (i.e., a potential core) where there is no mixing with the sample in the cell is formed, and the detection area is set in the interior of this cone. This allows measurement of the sample unaffected by foreign matter in the cell. The Model SNS-20's sectional area for detection is 2 mm by 0.4 mm and the inner diameter of the nozzle is 3 mm. Accordingly, a sample volume of 5 ml/min is attained.

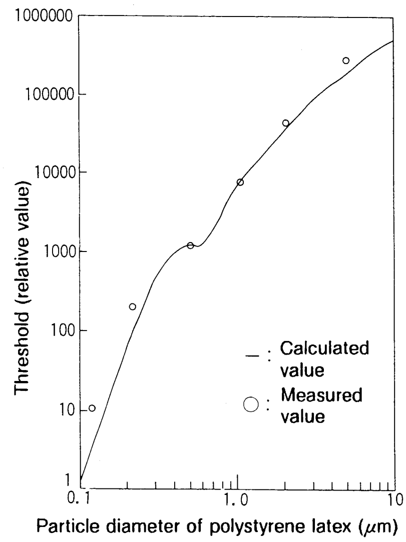


Fig. 7 Pulse-height characteristics vs. particle diameter of polystyrene particles in pure water

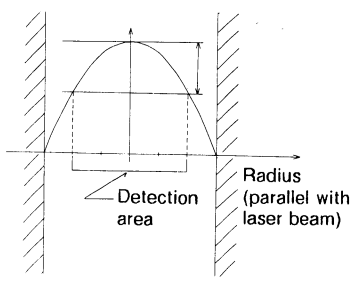


Fig. 8 Velocity distribution inside nozzle

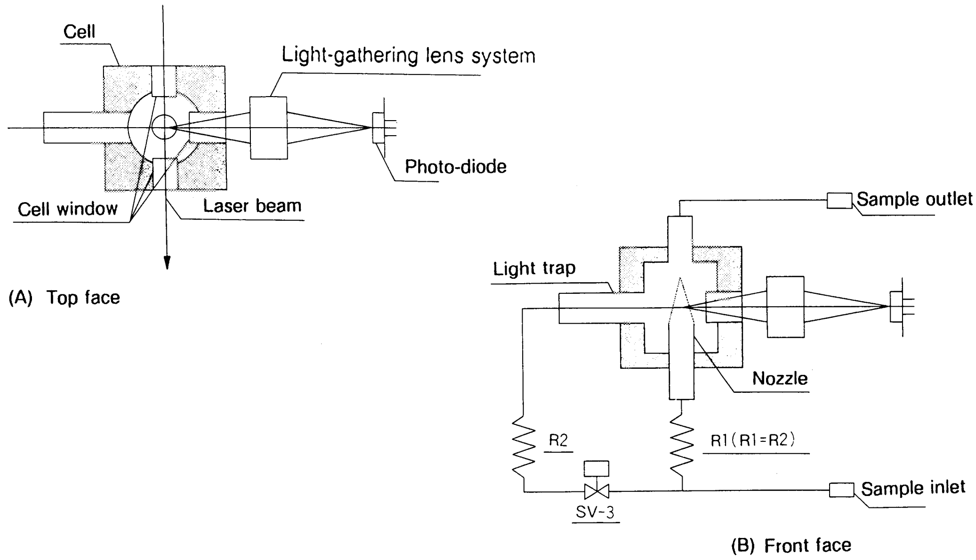


Fig. 9 Arreangement of sample flow and the detection area

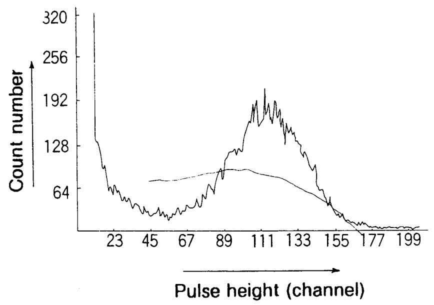


Fig. 10 Puls-height response distribution for standard particles (PSL 1.04 μm)

4.5 Pulse-Height Distribution with Standard Particles (PSL)

The pulse-height distribution with monodisperse particles indicates a rough resolution of the particle size. Fig. 10 shows the result obtained by actually measuring PSL particles with a particle size of 1.04 μm by the Model SNS-20.

5. SYSTEM CALIBRATION

Like air-particle counters, liquid-particle counters are calibrated using PSL as standard particles and deionized water for solvent. The standard solution is normally maintained at a high concentration, which should be verified in advance by using a scanning electron microscope (SEM). To calibrate the counter under 1 μm, use the method based on JIS K 0554, as shown in Fig. 11. Calibration over 2 μm is carried out with a pressurizing sampler in accordance with JIS B 9930. Since the use of the partial-measurement type cell causes fluctuation in adjustments, calibration must be carried out starting with the sample volume.

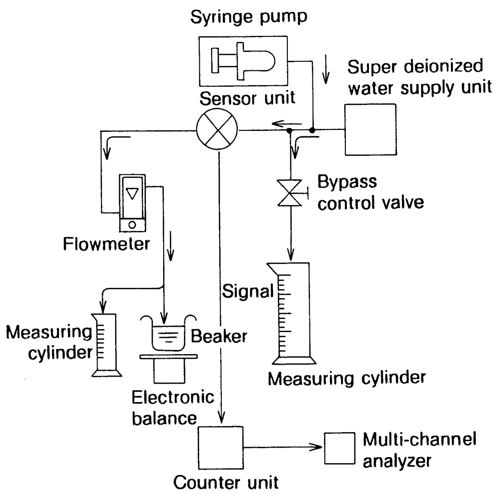


Fig. 11 Calibration flow

5.1 Calibration of Sample Volume

A standard solution with known concentration, e.g., with a particle size of 1 μm and a concentration of C particles/mℓ, is sent to the sensor unit as described above. Using a multi-channel analyzer (MCA), the data for the pulse-height distribution as described in 4.5 is obtained from the sensor output. The integrated value per minute, N, for the convex portion of the curve is obtained, and then the sample volume, M, is calculated using equation (1).

$$M = \frac{N}{C} \ (\mathrm{m}\ell/\mathrm{min}) \qquad \cdots\cdots \quad (1)$$

5.2 Calibration of Threshold (Voltage) Corresponding to Particle Size

First, the combination of particle sizes is determined; for the Model SNS-20, six particle sizes are used: 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 μm. Next, the commercially available standard particles with the particle sizes closest to the above values are selected to prepare a high-concentration primary standard solution. This solution is diluted, and then the secondary standard solution with a known concentration of C' particles/ml is sent to the sensor unit.

$$N' = C' \times M \times \frac{1}{2} \quad \cdots\cdots \quad (2)$$

where N' is the count per minute.

The threshold which would lead to N' obtained from equation (2) is obtained by changing the voltage value specified for the counter unit. The voltage value at this time is used as the calibrated threshold which corresponds to the particle size. A constant of 1/2 is included here because the half- count method* is used. See Fig. 12.

* Half-count method
Generally, when pulse height corresponds to some physical value, e.g., particle energy or particle size, and there is an approximately proportional relation between the physical value and the pulse height, i.e., a certain pulse height corresponding to a certain physical value. In actual cases, however, the pulse-height distribution has dispersion due to certain factors, and an axis-symmetrical distribution is often obtained. If the distribution is symmetrical, the threshold at the mid-point of the total integrated values will match the threshold at the peak of the distribution. Conversely, the half-count method uses this to consider the threshold at the middle of the distribution as the threshold at the peak of the distribution.

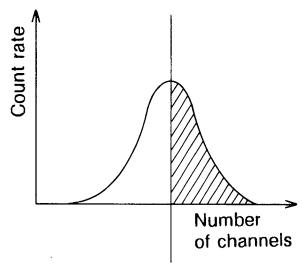


Fig. 12 Half count method

6. SUMMARY

The overview, measuring principle, calibration method, and other features of the Model PLCA-700 liquid-particle counter have been described. We can expect that industrial technology will advance further not only in the semiconductor industry but also in the precision machinery industry and in the optical technology industry. Liquid-particle counters that support these high-level technologies must be ever more reliable. It is intended that the technology introduced here will contribute materially to this purpose.

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