

Measurement of Particle Concentrations in Central Chemical Delivery Systems

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ABSTRACT

This article evaluates recently developed high sensitivity optical particle counters for measuring particle concentrations in high purity semiconductor process chemicals. The results indicate that use of these low sampling rate counters is appropriate for obtaining accurate measurements. The results also indicate that particles in these chemicals may come from two sources: small particles that pass through the filters used to purify the chemicals and larger particles that originate at or downstream of the filter.

INTRODUCTION

The concentrations of particles in semiconductor process chemicals supplied by central chemical delivery systems can be measured using optical particle counters (OPCs).^{1,2} Semiconductor manufacturers presently require control of particles greater than 0.3 to 0.5 μm in diameter. However, future needs of the industry will necessitate control of smaller and smaller particles.

Particle concentrations in chemicals usually increase with decreasing particle size. The size distribution of the particles can often be described using a power law distribution with a slope of -2 to -3 .³ Although this distribution will probably overpredict the number of very small particles, it is thought to be applicable for particles $\geq 0.05 \mu\text{m}$ in diameter. A power law distribution with a slope of -3 predicts that a solution which contains 1 particle/ml $>0.5 \mu\text{m}$ contains 125 particles/ml $>0.1 \mu\text{m}$.

The chemicals supplied by state of the art central chemical delivery systems typically contain very low levels of particles $>0.3 \mu\text{m}$ in diameter, sometimes at or near the background noise level of the particle counting instruments presently used.⁴ When the particle concentrations are at or near the instrument background level, accurate determination of the particle concentration and variations in particle concentration with time are difficult to determine. Hence, it is difficult to further reduce particle concentrations in chemicals.

The difficulty in accurately determining particle concentrations in present central chemical delivery systems, combined with the growing need to control smaller particles, means that instruments with higher sensitivi-

ties are required. The increased sensitivity needed to detect smaller particles can be gained by using smaller sensor sampling volumes. However, the result is reduced sampling rates. Only if the increased particle concentration at the smaller particle size is sufficient to outweigh the counting rate loss due to low sampling rate is the use of a more sensitive instrument beneficial.

Several new OPCs made by various manufacturers are on the market. Because these instruments have different operating characteristics, a brief survey was undertaken to determine the state of the art in sensor technology. Sensors from three manufacturers were included. This article compares the manufacturers' claimed performance of these counters and examines their ability to measure particles in chemicals supplied by central chemical delivery systems. No attempt was made to verify the manufacturers' claims.

SENSOR DESCRIPTION

OPCs detect and size particles by measuring the amount of light scattered by individual particles as they pass through a beam of light. The amount of light scattered is related to the size of the particle with smaller particles scattering less light. For particles larger than about 5 μm , scattering is proportional to the particle diameter squared (geometric scattering). For particles from approximately 0.2 to 5 μm in diameter, the amount of light scattered is proportional to the particle diameter to the second to the sixth power (Mie scattering).

For particles smaller than approximately 0.2 μm in diameter, scattering is proportional to the particle diameter to the sixth power (Rayleigh Scattering). The exact relationship between the amount of light scattered and the particle diameter is a complex function of the scattering angle, the medium and particle refractive indexes, and the wavelength of the light source.⁵

Because scattering of light by small particles decreases dramatically with decreasing particle size, the difficulty in detecting small particles is in obtaining an acceptable signal-to-noise (S/N) ratio. Techniques used to increase the S/N include increasing the intensity of the illuminating light and decreasing the background noise. The background noise is a combination of stray scattered light, molecular scattering by the fluid medium, and electrical noise originating from the light source, light

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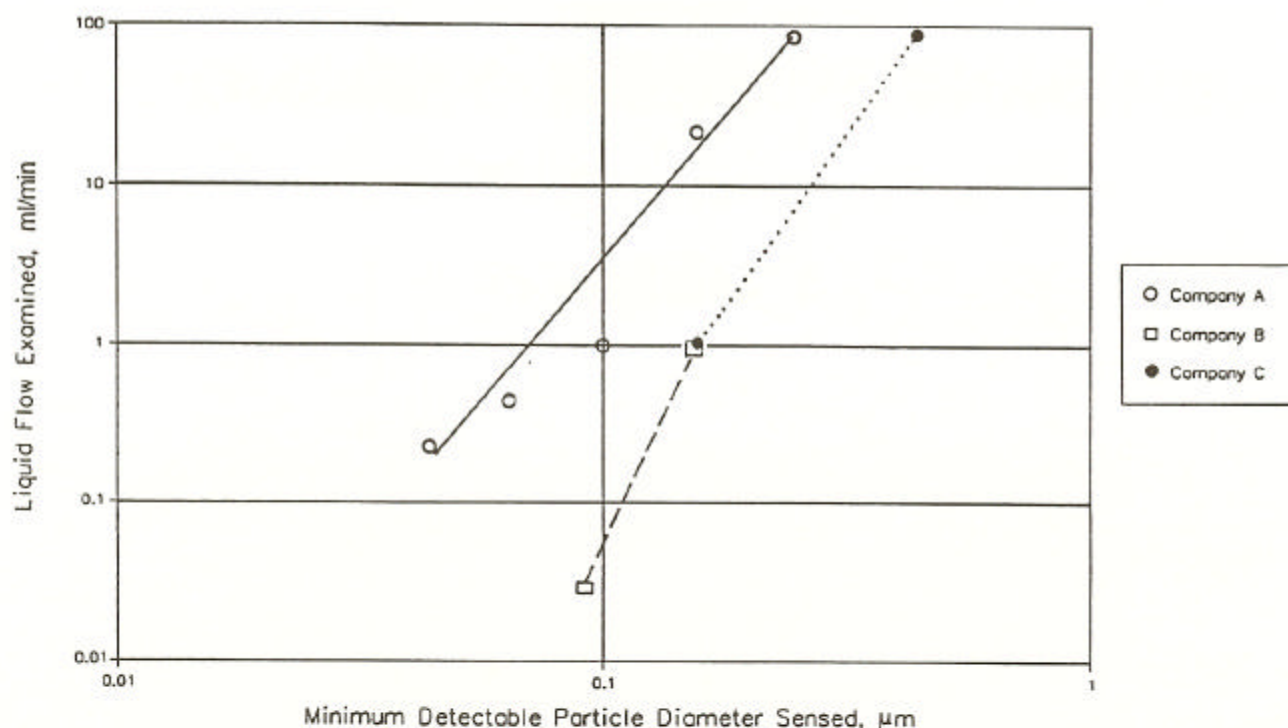


Figure 1. Comparison of commercially available high sensitivity light scattering particle counters.

detector, amplifiers, etc. Thus, the limiting noise source is a function of the optics and electronics of the OPC sensor used.

Two types of OPC sensors are commonly used to detect particles smaller than $0.5 \mu\text{m}$ in diameter in liquids: volumetric and in situ. Both have laser light sources. Volumetric sensors examine all of the fluid flowing through the sensor cell; in situ sensors examine only a small portion of the flow through the sensor cell by focusing the light source onto a small region in the center of the fluid flow path.

In situ sensors offer the advantage of increased light intensity in the sensing volume as the laser beam is focused on a small volume. In addition, in situ sensors have decreased background noise because the amount of stray scattered light reaching the sensor collection optics is smaller than that in volumetric sensors. The reduced scattered light collected is a result of separating the particle sensing volume from the interface between the cell wall and the fluid. These advantages result in increased instrument sensitivity. However, the viewing volume in these sensors is less well defined than that of volumetric sensors. Large errors can result if the viewing volume is inaccurately defined.

In situ sensors can be further divided into spectrometers and monitors. In spectrometers, the sensing volume is accurately defined. Consequently, these instruments can be used to accurately determine particle size and number. Monitors are less accurate (and less expensive) but can detect the presence of smaller particles. In addition, the concentrations measured with monitors tend to be higher than the actual concentration.^{6,7} This occurs because large particles that pass through the laser

beam outside the viewing volume scatter enough light to be detected as small particles. This does not occur in spectrometers because the viewing volume is better defined.

Table 1 lists the sensors surveyed in this study. Volumetric sensors, in situ monitors, and in situ spectrometers were included. Ten sensors from three companies were examined. The table includes the manufacturers' claims for minimum detectable particle size and sample flow rate.

THEORETICAL SENSOR ANALYSIS

Particle counting is governed by Poisson statistics that describe the counting of random events. In Poisson statistics, the standard deviation of a measurement is related to the square root of the number of events counted. The larger the number of events counted, the smaller the variation. Hence, rapid sampling rates are desired to reduce sample variation. Rapid counting rates are obtained by using high sampling rates.

The relationships between the smallest particle size detectable and the sampling flow rate for the sensors examined are shown in Figure 1. It shows the instrument manufacturer claims of sensitivity and flow rates along with power fits of the data for each of the three manufacturers. The graph indicates that the technology used by company A is superior to companies B and C because company A sensors sample at 10 to 20 times the rate of the other sensors. The superiority of company A sensing technology is believed to be related to the method used to view the sampling volume.

Table 1. Description of Sensors Surveyed Data Based Upon Manufacturers' Claims

Company	Sensor Type ¹	Minimum Detectable Diameter, μm	Sampling Rate, ml/min	Comments
A	V	0.30	75	Water only
	S	0.20	25	
	S	0.10	1	
	M	0.10	1	
	M	0.065	0.45	
	M	0.05	0.25	
B	V	0.50	75	
	M	0.20	1	
C	M	0.20	0.88	Water only
	M	0.065	0.025	

V = Volumetric sensor
 S = In situ spectrometer
 M = In situ monitor

The lines in Figure 1 represent least square power fits of the data presented:

$$F_S = A_0 D_{PS}^{A_1} \quad (1)$$

where:

F_S = liquid flow examined, ml/min
 D_{PS} = minimum detectable particle diameter, μm
 A_0, A_1 = constants

Note that F_S represents the flow rate through the sensor sampling volume, not the flow rate through the sensor cell.

The constants for the power fits for the three companies included in this study were

Company	A_0	A_1
A	4010	3.3
B	710	4.2
C	2710	4.9

The slopes of the lines in Figure 1 (constant A_1) represent the rate at which the sensed flow rate decreases with sensor increased sensitivity. The slopes shown range from 3.3 to 4.9; that for Company A is 3.3. Thus, the sampling rate for company A technology decreases with the 3.3 power with respect to decreasing particle diameter detection.

The slope for company A technology is less than that of companies B and C. Hence, the use of this technology results in a slower decrease in sampling volume with increasing sensitivity.

Using particle counters with increased sensitivity to measure clean fluids will not offer an advantage unless the number of particles in the fluid increases at a rate faster than the sampling volume decreases. If this is not true, the counting rate will decrease as instrument sensitivity increases.

Particle size distributions in chemicals often follow a power law distribution:

$$N = A_2 D_P^{A_3} \quad (2)$$

where:

D_P = particle diameter, μm
 N = particle concentration, no./ml
 A_2, A_3 = constants

The instrument counting rate in counts per minute (C_R) is equal to the product of the instrument sampling rate and the particle concentration:

$$C_R = F_S * N \quad (3)$$

Substitution of Equations 1 and 2 into Equation 3 and evaluating the resulting equation at D_{PS} yields the instrument counting rate as a function of the minimum detectable particle diameter:

$$C_R = A_0 A_2 D_{PS}^{(A_1 + A_3)} \quad (4)$$

Equation 4 indicates that unless $A_1 + A_3$ is negative, the instrument counting rate will decrease with decreasing particle size. For example, if company A sensors are used, A_3 must be < -3.3 (i.e., $-4, -5$, etc.) for the instrument counting rate to increase when more sensitive sensors are used. This is shown pictorially in Figure 2, which presents the expected counting rates of company A equipment assuming different values for A_3 . The graph was prepared assuming 1 particle/ml $> 0.3 \mu\text{m}$.

Experiments performed in the past have indicated particle size distribution slopes ranging from -2 to -3 . Hence, it could be concluded that less counts would be obtained using more sensitive instruments. However, these measurements were made using instruments that measure particles $> 0.3 \mu\text{m}$ and the chemicals were filtered using $0.2 \mu\text{m}$ filters. These filters are extremely effective at removing particles $> 0.3 \mu\text{m}$ in diameter. Hence, the particles downstream of the filters $> 0.3 \mu\text{m}$ probably come from sources other than the incoming chemical. Also, the filter particle removal efficiency decreases rapidly for particles $< 0.25 \mu\text{m}$. Therefore, it might be expected that two distributions of particles exist in filtered chemicals: one from particles passing through the filters; and one from sources downstream of the filters. Furthermore, the number of particles smaller than the rated filter pore size should increase very rapidly due to the decreasing filter capture efficiency.

APPLICABILITY OF HIGH SENSITIVITY SENSORS

In order to determine the particle size distribution of small particles in state of the art chemical distribution systems, measurements were made in several chemicals using a PMS HSLIS, an in situ spectrometer with a minimum detectable particle diameter of $0.1 \mu\text{m}$. Measurements were made in DI water, HCL, and NH_4OH . The average concentration obtained during a 1 hr sample

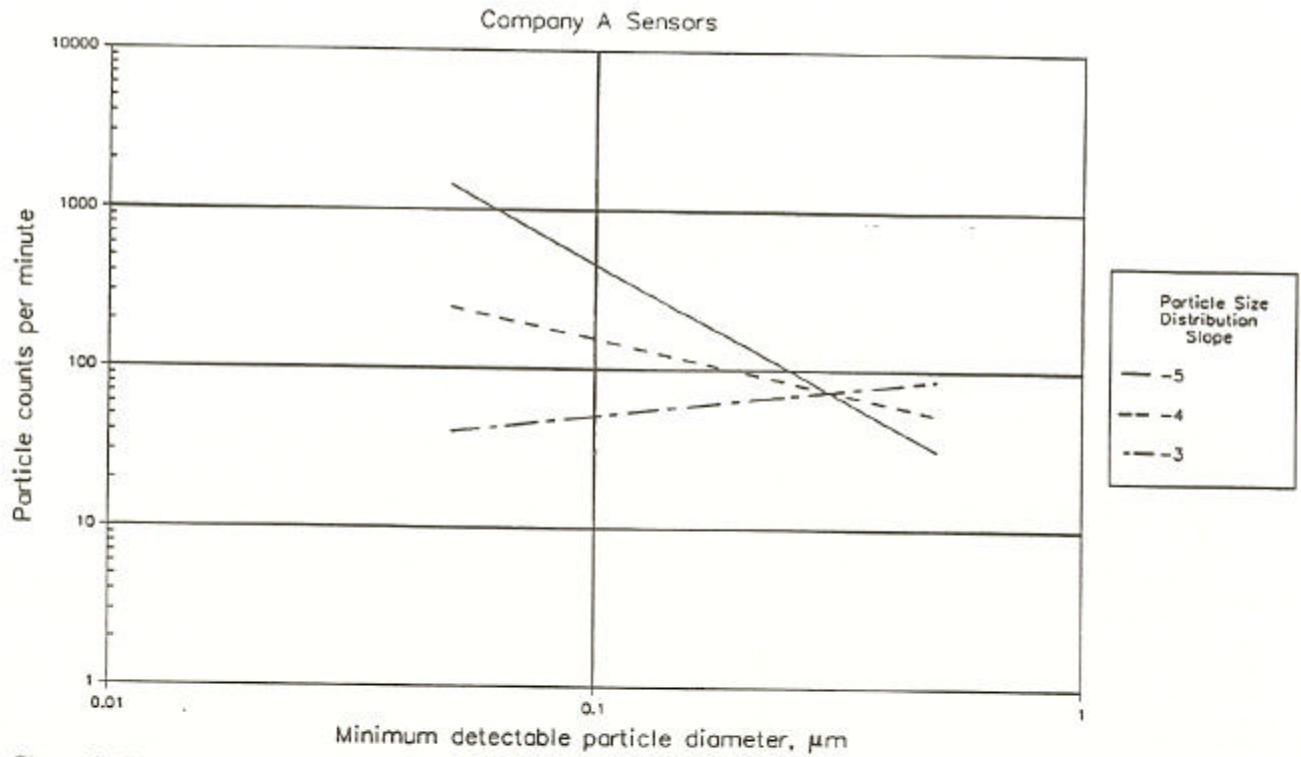


Figure 2. The effect of particle size distribution slope of instrument counting rate.

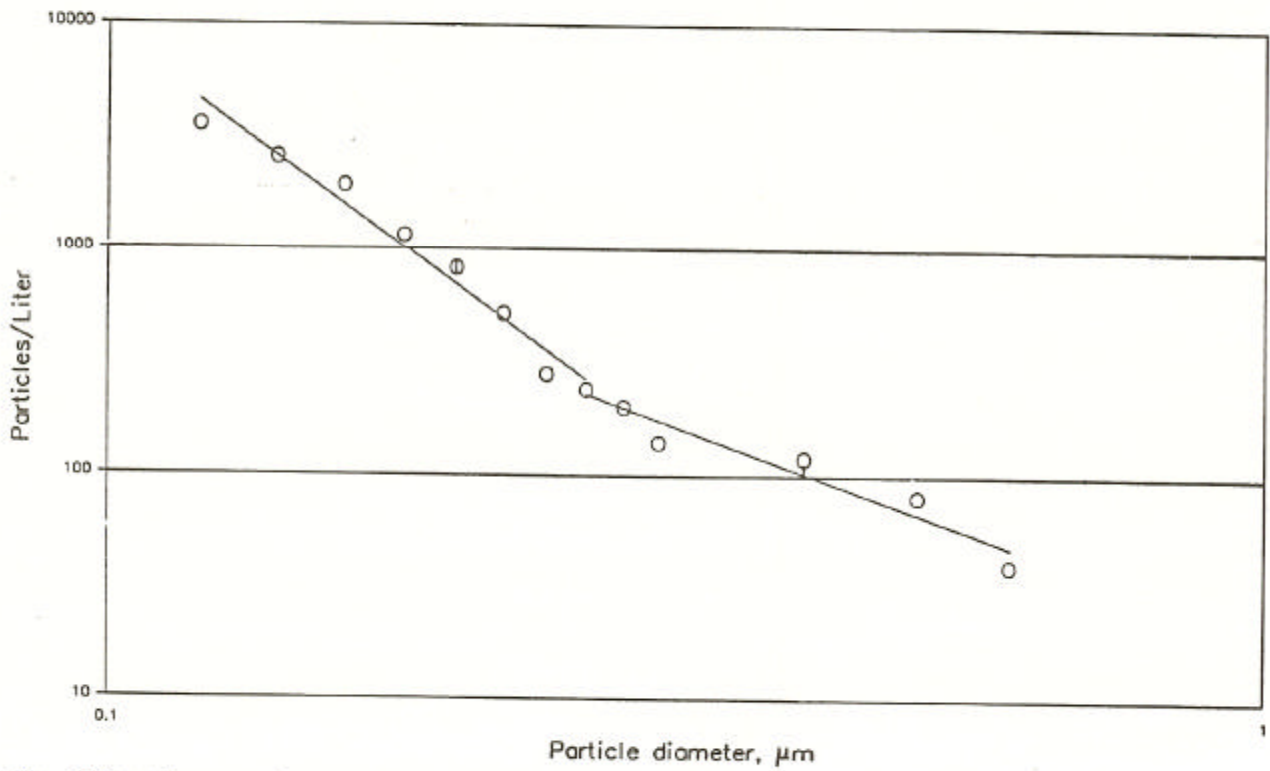


Figure 3. Particle concentrations measured in DI water using a high sensitivity optical particle counter (PMS HSLIS)

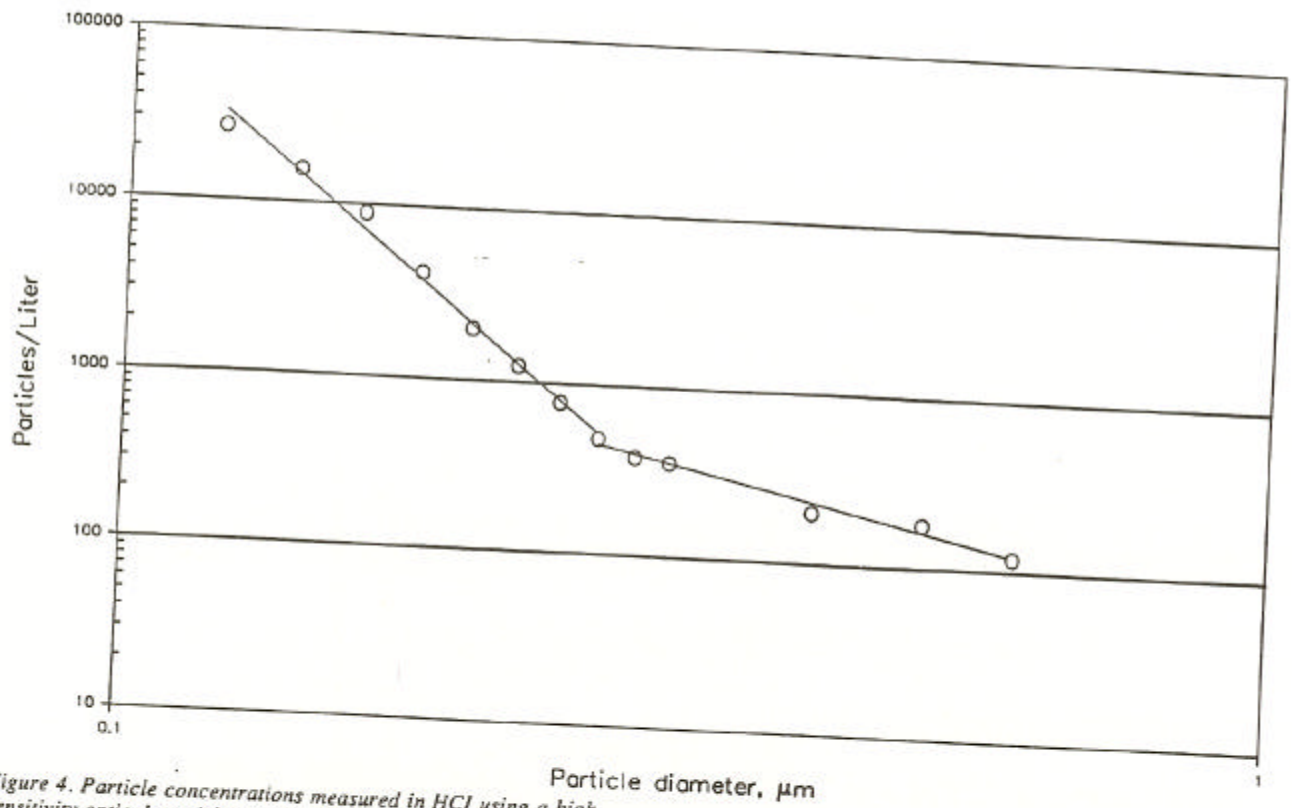


Figure 4. Particle concentrations measured in HCl using a high sensitivity optical particle counter (PMS HSLIS).

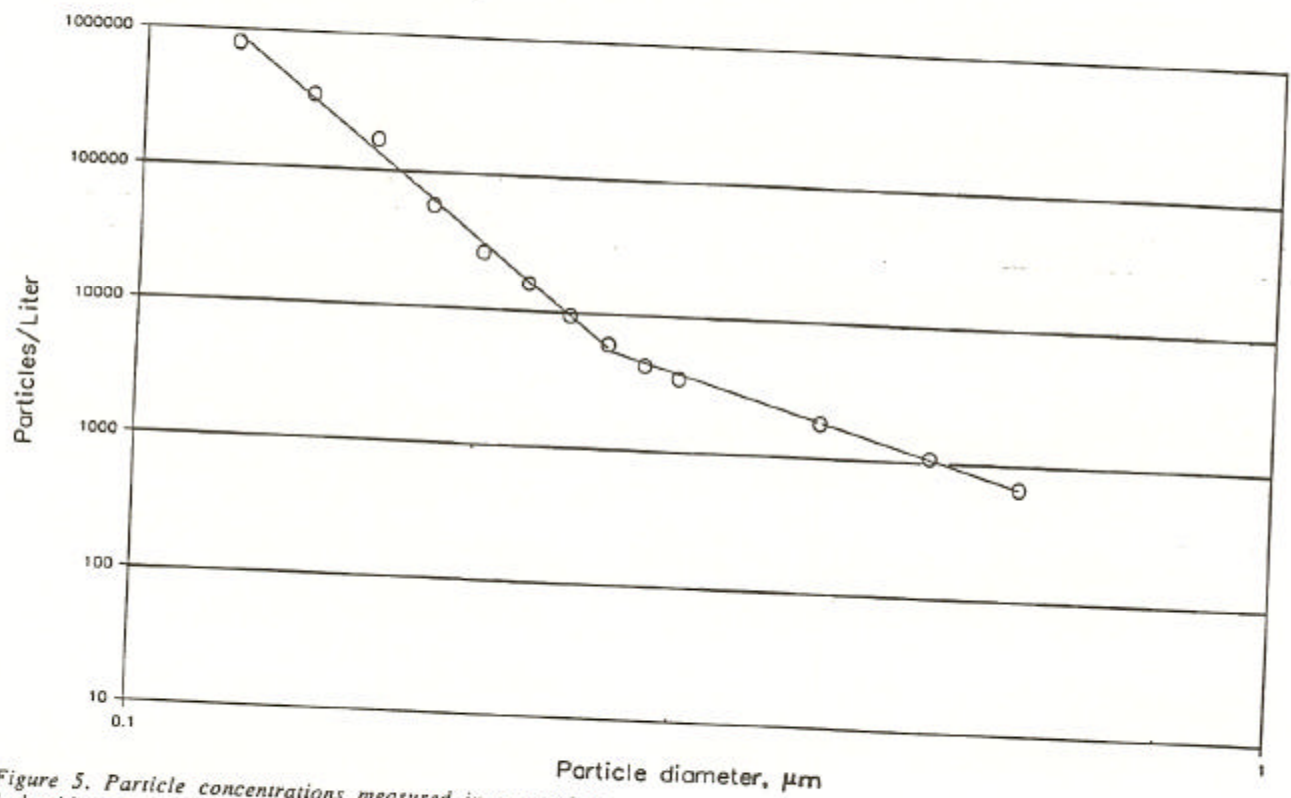


Figure 5. Particle concentrations measured in ammonium hydroxide using a high sensitivity optical particle counter (PMS HSLIS).

taken after 3 to 8 hr of system operation are shown in Figures 3 through 5.

Figures 3 through 5 indicate a discontinuity in the particle size distribution that occurs between 0.2 and 0.3 μm . The slopes of the power law distributions for particles $>0.26 \mu\text{m}$ vary from -1.6 to -2.5 while the slopes for particles $<0.26 \mu\text{m}$ vary from -3.7 to -6.4 as shown in Table 2.

Table 2. Slopes of Particle Size Distributions Measured Using a PMS HSLIS In Situ Spectrometer

Fluid	Particle Size Distribution Slope	
	Particles $>0.26 \mu\text{m}$	Particles $<0.26 \mu\text{m}$
Water	-1.9 (-2.3)*	-3.7
HCl	-1.6 (-2.8)*	-5.4
NH ₄ OH	-2.5 (-2.1)*	-6.4

*Numbers in parentheses were obtained using a PMS IMOLV particle counter and are included for comparison.

The results described in Figures 3 through 5 indicate that the use of high sensitivity particle counters made by company A is appropriate because the slopes for particles smaller than $0.26 \mu\text{m}$ are <-3.3 for measurement of very clean chemicals. Less benefit is obtained by using high sensitivity sensors from companies B and C because of the faster decrease in sampling volume with increasing sensitivity.

The data in Figures 3 through 5 also support the two particle population theory, at least for chemicals filtered with $0.2 \mu\text{m}$ filters. It appears that particle sources at or downstream of the filter have a size distribution with a power law slope of -2 to -3 . The distribution of the small particles passing through the filter appears to have a power law slope of -4 to -6 .

One word of caution: the HSLIS data presented in Figures 3 through 5 are a result of limited sampling. Also, the data from the HSLIS did not agree well with those obtained using a PMS IMOLV, a volumetric sensor that has been used in multiple chemical particle studies with reliable, repeatable results. The reason for the discrepancy between the two sensors is thought to result because the sensors have different optical designs.¹² The differences in optical designs mean that the sensors will respond differently to particles with refractive indexes that vary from those of the PSL particles used to calibrate the sensors. Additional data are needed to solidify these hypotheses.

SUMMARY

An evaluation of commercially available high sensitivity optical particle counters was performed to assess the utility of these instruments for measuring particle concentrations in high purity semiconductor process chemicals. It was shown that there is a relationship between the minimum particle size detectable and the sensor sampling volume, with the sampling volume proportional to the third or fourth power of the minimum detectable particle diameter.

It was shown that there are large differences between the sensing technology used by different particle counter companies. Sampling rates for sensors having the same minimum detectable particle diameter varied by a factor of 10 to 20.

Data obtained using a sensor with a $0.1 \mu\text{m}$ minimum detectable particle diameter indicated that the use of high sensitivity sensors is appropriate for obtaining accurate measurements of particle concentrations in high purity semiconductor process chemicals. The data also indicated that there may be two sources of particles in the chemicals: one due to sources at or downstream of the filters used to remove particles from the chemicals, and one due to passage of small particles through the filters.

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