Monitoring Particles in Process Chemicals

Introduction

High particle levels in process chemicals have been shown to directly affect product quality. The need for continued reductions in particle size and quantity in cleanroom environments is well established. The International Technology Roadmap for Semiconductors (ITRS), sponsored by the United States Semiconductor Industry Association (SIA), defines the need for persistent decreases in particle levels in process gases, water, chemicals, and air in order to meet future generation technology nodes. The ability to accurately measure these contaminants is the first step in developing a comprehensive particle control plan.

Principles of Operation

While numerous techniques are available to monitor and characterize particulates, most require significant off-line analysis and interpretation. This usually reduces the number of measured samples resulting in fewer data points and time delayed results. Liquid Particle Counters (LPCs), based on light scattering, are widely used for continuous on-line monitoring of process chemicals. Proper selection and implementation of an LPC are important for ensuring data integrity.

Although the design, performance, and specifications of LPCs may differ, a few key principles remain the same. First, particle counters do not directly count particles. Particle counters based on light scattering are designed to measure the equivalent optical size of particles as referenced against a calibration standard. In most cases, that standard is a polystyrene latex sphere (PSL). These are readily available and National Institute of Standards and Technology (NIST) size traceable.

Laser light, with wavelengths usually between 600-800 nm, is used to illuminate the sample cell or capillary. As individual particles traverse the laser beam, light scattering occurs because of the index of refraction difference between the transport media and the particle. The amount of scatter depends on many factors but is largely dependent on the particle size, shape, and index of refraction. Scattered light is then collected and focused onto a photodetector where the signal is converted into an electronic pulse (**Figure 1**).

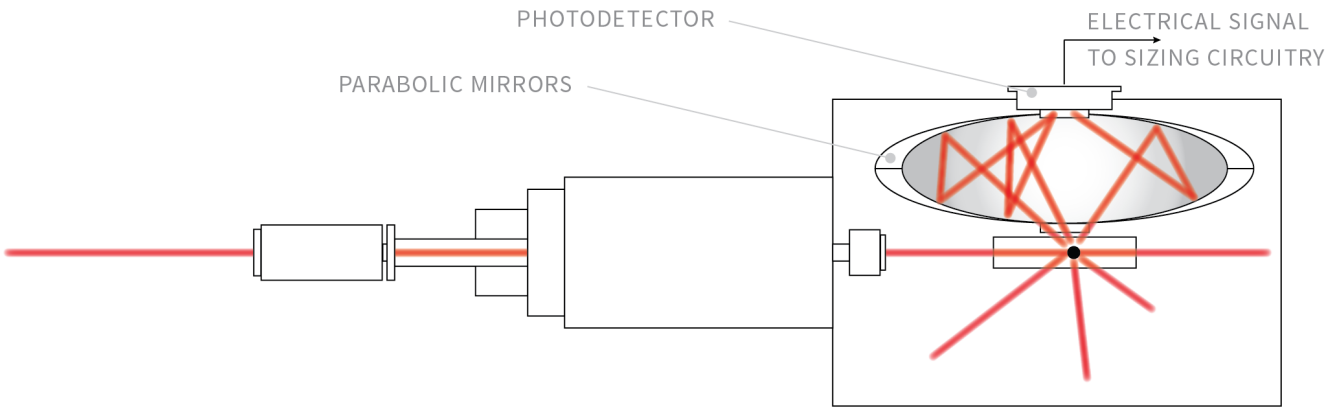


FIGURE 1 Illustration showing the principle operation of a Liquid Particle Counter

The dashed lines (**Figure 2**) represent the voltage values or channels defined for each particle size during calibration with PSLs. Each pulse represents an individual particle, while the magnitude of the pulse determines its size by comparing the PSL equivalent amount of scatter.

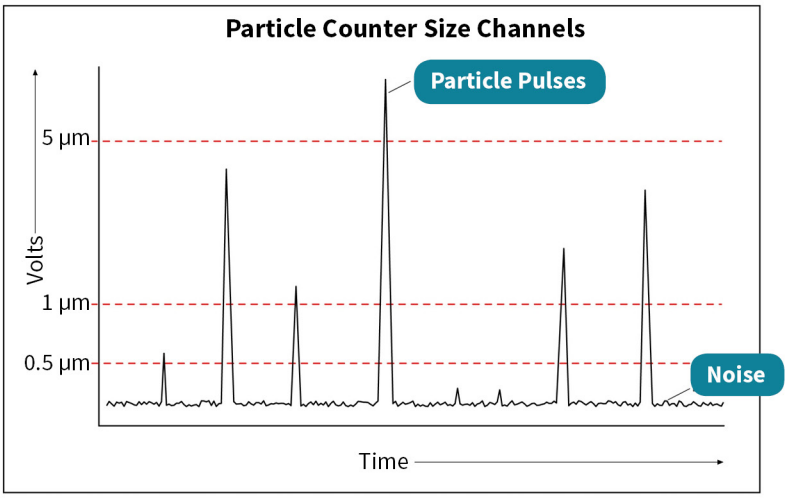


FIGURE 2 Electron pulses from photodetector showing six distinct particles of various sizes

Selecting the Right Instrument

There are a few key things to consider when selecting a particle counter for your application:

- Sample Volume
- Resolution
- Sensitivity

Sample Volume: Liquid particle counters can be classified as either volumetric or nonvolumetric. The terms refer to the sample percentage illuminated by the laser beam in the sampling region or capillary during operation.

In volumetric counters the beam is shaped such that its intensity is mostly uniform across the capillary. Because the energy intensity profile of a laser is Gaussian shaped, the beam span in volumetric counters is significantly wider than the capillary. This has the effect of producing a uniform beam so that the traversing particle is exposed to the same amount of light energy regardless of where the particle is located in the flow path, improving resolution. Since 100% of the capillary is uniformly illuminated, all particles larger than the sensitivity limit of the instrument are counted. State-of-the-art volumetric counters can detect particles as small as 0.1 µm. These are used to monitor process baths, for incoming quality control checks, as well as for some process chemicals.

In order to increase the sensitivity of an LPC the background light scatter from the capillary must be eliminated. By removing the capillary the laser beam is then focused and shaped in such a way that only a very intense portion of the beam illuminates a very small portion of the total flow, greatly improving the signal to noise ratio. The result is a significant improvement in instrument sensitivity. State-of-the-art nonvolumetric counters can detect

particles as small as 0.05 µm. However, the decrease in sample volume greatly reduces resolution. Non-volumetric counters are typically only used to monitor DI water and some extremely clean process chemicals. These counters tend to produce poorer instrument-to-instrument matching and should only be compared using total cumulative counts.



FIGURE 3 Chem 20™, an example of a volumetric particle counter

Resolution is defined as the ability to distinguish particles of various sizes. For example, an instrument with very good resolution, a spectrometer, would be able to resolve the difference between a 0.8 µm and 0.9 µm particle. Instruments with average resolution would consider the particles to be of similar size. Volumetric counters provide great resolution and hence offer a large number of user selectable size channels. In contrast, many non-volumetric counters offer a few very broad size channels that are manufacturer defined.

Sensitivity is defined as the smallest detectable particle size for a given instrument. End users often request the instrument with the highest sensitivity. This is usually impractical for two reasons. First, only a handful of process chemicals are truly clean enough to justify the highest level of detection. Secondly, incremental improvements in sensitivity require a significant improvement in the signal-to-noise ratio, increasing instrument costs.



FIGURE 4 LiQuilaz® II, an example of a liquid spectrometer

Data Quality Assurance

After carefully considering the factors influencing the proper choice of a particle counter, the next step is the implementation process. Experience has shown that this process is often overlooked. Follow the steps outlined below to be sure that the results from an LPC are stable, accurate, and repeatable. These recommendations should be viewed in their entirety; unless all aspects are considered, the data may be suspect.

1. Sample Point
2. Filtration
3. Particle Size Distribution
4. Flow Rate Control
5. Coincidence Loss and Saturation
6. Background Scattering
7. Zero Counting
8. Bubbles
9. Molecules and Colors

Sample Point

Thought should be given to the particle monitoring location in the process flow. All components that contact the process chemical such as valves, tubing, filters, and pumps will contribute particles, sometimes significantly. Only high quality fluid components should be used where particle levels are monitored. Numerous methods exist for monitoring process chemicals in a manufacturing environment.

For continuous online monitoring, LPCs are typically located downstream of most filtration processes and tend to provide the most stable and repeatable results. Whenever upstream components are changed the system should be given ample time to clean-up before particle monitoring is continued.

Off-line batch sampling requires special attention as sample containers and handling can cause poor data repeatability and reproducibility. It is important to be able to demonstrate clean and repeatable background counts with de-ionized water before the chemical of interest is sampled.

Filtration: It is always recommended to filter your process chemicals below the sensitivity limit of the particle counter whenever possible. Because particles slightly smaller than the sensitivity limit can affect background scattering and potentially coincidence, a good manufacturing practice should include filtration well below the sensitivity limit.

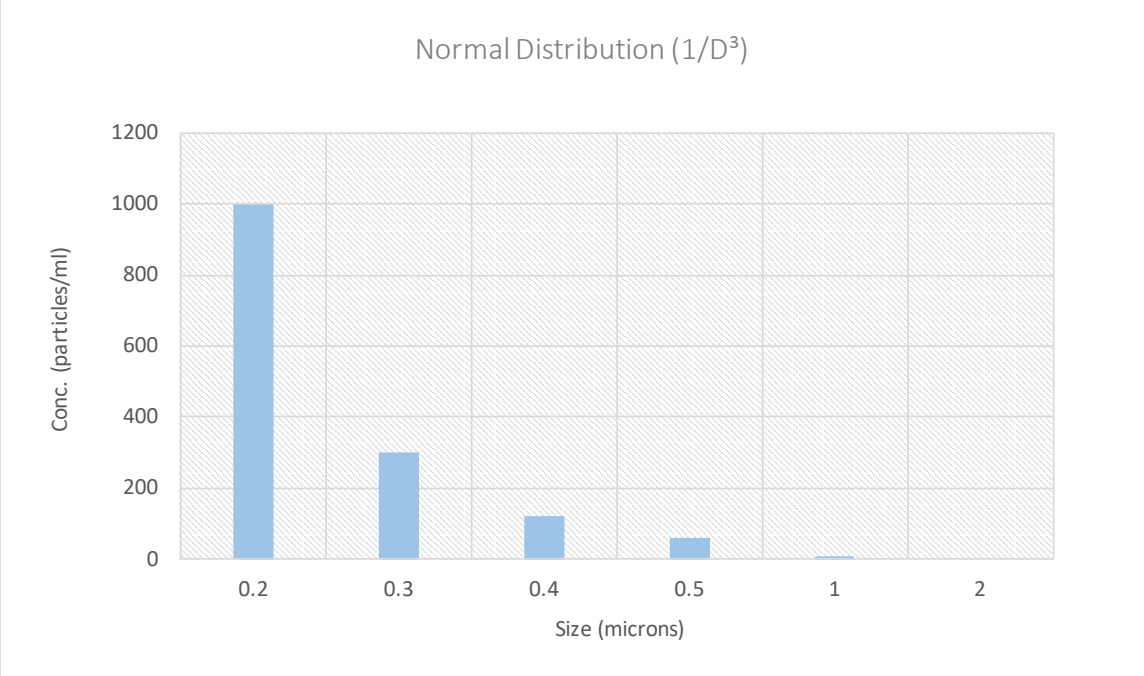


FIGURE 5 Typical liquid particle distribution

Particle Size Distributions

Years of particle counting experience analyzing customer data shows that most ambient particle distributions in continuously filtered liquid systems follow a D^{-3} size distribution (where D = particle diameter) on total cumulative counts. **Figure 5** shows a typical particle distribution in liquid systems. In extremely clean DI water systems, the distribution can be steeper (D^{-4}), and in dirty systems, the distribution can be flatter (D^{-2}). It is equally important that the distribution remains consistent from sample to sample.

When analyzing particle data, it is essential to ensure that this type of particle distribution is present. Deviations from this type of ratio should immediately alert the user to a potential problem.

Flow Rate Control

All LPCs have a flow rate specification and are calibrated at a precise flow. This means that real-world particles are intended to pass through the particle counter at the calibrated flow rate. If the proper flow rate is not maintained, both sizing and counting accuracy are compromised. The resident time of a particle as it traverses the laser beam has an appreciable effect on the amount of light scattered. If the flow rate is set too high, the electronics do not have sufficient time to fully integrate the signal, compromising sizing accuracy. Counting accuracy is compromised because the resulting signal is now too small to exceed the particle size threshold. Further complicating the issue, is that the accompanying software is normalizing the data to the calibrated flow rate. Conversely, if the flow rate is too slow, the transit time is increased and the particle appears to be larger than its actual size. It is critical that each LPC is controlled to the calibrated flow rate.

Coincidence Loss and Saturation

LPCs are often referred to as Single Particle Optical Sensors (SPOSs) because they are designed specifically to detect and analyze a single particle at a time. Situations where more than one particle traverses the laser beam are possible in process chemicals with high levels of particles. In these situations, multiple traversing particles can be counted as a single large particle or undercounting can occur if these particles are aligned in the beam pathway. This is defined as coincidence loss and varies by instrument type and manufacturer. For example, the specification may be 10% coincidence loss at greater than 10,000 particles/mL. This means that 10% of the particles are being lost at this concentration. Also, this phenomenon is not linear or predictable enough to make conclusions about the actual total number of counts once the manufacturer's maximum concentration is reached. This can be seen in the data by looking at differential counts and observing a flattening of the distribution at the smaller size channels. If the concentration becomes too great, the instrument electronics themselves become saturated and can no longer integrate each pulse independently leading to numerous errors.

Background Scattering

Contamination of the capillary walls is the leading cause of excess scattering in LPCs. If severely contaminated or scratched, the amount of scatter coming from capillary can equal the amount of scatter from the smallest detectable particle size. There are typically two ways to recognize whether this is occurring. First, the accompanying software reports the amount of background scatter. Each LPC has a specification for this value. Once this value has been exceeded, the collected data should be considered suspect.

Additionally, this can often be seen in the data. If the amount of scatter from contamination equals the amount of scatter from the smallest detectable particle size, there will be an excessive number of counts in the first size channel. This will shift the PSD further to the left resulting in a significant departure from the typical D^{-3} relationship.

Zero Counting

A technique known as zero counting is a good troubleshooting tool for process chemical monitoring. De-ionized water is typically much cleaner than process chemicals and can therefore be used to baseline your instrument. Once you have an established baseline, at any point you suspect a problem you can re-run the zero count test for instrument verification.



FIGURE 6 CLS-700T, an example of a bubble compression system

Bubbles

Bubbles in liquid systems will scatter light due to the index of refraction contrast between the liquid media and air. Usually, the amount of scatter is significant enough to be recorded as a particle and often in the larger size channels. Bubbles can come in two forms, naturally occurring bubbles due to dissolved gases and process chemistry and artificially created bubbles due to poor handling techniques. Issues with

naturally occurring bubbles can be exasperated by the action of creating vacuum during syringe sampling. Online or compression LPCs should be used in these circumstances. Poor handling with viscous chemistries or chemicals with high level of surfactants can generate bubbles in such a way that the best method of dealing with this is preventing bubbles from forming in the first place by improving handling practices.

Molecules and Colors

Other concerns with chemicals can include very large molecules, fluid color, or miscibility. These phenomenon can scatter light which may further complicate obtaining reasonable results with a LPC, making it all the more important that the appropriate particle counter is used and that the user fully understands the results being generated.

Conclusion

Selecting the appropriate Liquid Particle Counter and generating quality data is critical for process control. It is important to match the appropriate LPC sensitivity, type, and sampling technique to the chemical of interest. Additionally, the user must understand the fundamentals of optical particle counters and the properties of their process chemicals to ensure a valid measurement.

References

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App Note 80 01.2019