Particle Size and Concentration Measurements for Real-Time Process Applications

Over a 20 year development period Process Metrix (and its predecessor, Insitec) have developed three types of optical in situ real-time particle instruments, which fall under two technical categories. The two types are ensemble (measuring the light scattering from a group of particles) and single particle counting (SPC). Instruments within these categories have differing performance characteristics depending primarily on size and concentration. Basically, ensemble methods are needed for high concentration applications, while SPC methods are required for low concentrations, with the dividing line typically being 1-10 ppm by volume. The choice of which type of instrument is most suitable for a given application is the subject of the following note.

The determining factor for the optimal instrument choice is primarily particle concentration, and secondarily particle size. This is certainly an absolute requirement for in-process measurements, where it is not possible to use dilution to match instrument operating requirements. In contrast, for laboratory measurements the user generally has the latitude to provide sufficient dilution to match limited instrument range. The downside of this laboratory flexibility is the time delay and the need for uncertain sample acquisition and handling, which can create uncertainties regarding sample integrity.

**Single particle counting** (SPC) optical instruments rely on passing one particle at a time through the optical sensing volume. For laboratory-based SPC instruments, this limit is approximately $10^3$-$10^4$ particles/cm$^3$. This corresponds to a volume concentration of about 1 part per million (PPM) for particles with a 10 micron median diameter, leading to an upper limit mass concentration of 0.3 gm/m$^3$ for unit density particles. For particles of 1 micron median diameter, this limit would be more in the range of 0.3 part per billion (PPB) by volume or 0.3 mg/m$^3$.

Process Metrix instruments emphasize the developing and future trend toward automated real-time in-process measurements. Figure 1 shows a general operating map for Process Metrix single particle counting and ensemble instruments. Note that the particle concentration range for all these instruments exceeds 15 orders of magnitude, along with 4 orders of magnitude in size range! It is no surprise that different instrument configurations will be required to accommodate this broad range of potential applications.

The **PPC SPC** technique for in situ measurements was developed to accommodate particle number concentrations up to $10^7$/cm$^3$ by using a small optical sample volume with a beam diameter of 10 microns. Based on our experience, this concentration appears to be a practical upper limit for SPC instruments. Cost, complexity, and practical physical limitations all conspire to put the maximum achievable limit for SPC instruments at less than $10^8$ particles/cm$^3$. Nevertheless, this is 3-4 orders of magnitude higher concentration than laboratory instruments! On a mass basis, this corresponds to a general limit of less than 5 gm/m$^3$ (5 ppm by volume) for typical particle distributions with median diameters less than 10 microns.
Primary applications include high temperature or pressure measurements in power generation boilers, gasifiers, and gas turbines. Other applications include petroleum processing with catalysts, and large scale industrial filtration processes. For a summary discussion of new applications to gas turbines and refinery expanders being developed by PMC in conjunction with DOE, see other application notes in the download list.

2.0 PPC Components and interfacing options

Figure 1. Process Particle Counter (PPC) standard system
The standard PPC system includes the following components:
1) PPC probe with standard flow window configuration (center section)
2) Laptop computer for data collection and processing
3) Ethernet cable (max. length 300 ft.)
4) PPC probe signal and power cables (max. length 20 ft)
5) Signal Processor enclosure.
Figure 2. High pressure flow cell for PPC. Instrument transmitter and receiver attach to front and back face. Process connections at right and left, high pressure purge connections at top and bottom, water cooling connections diagonal.

Figure 3. High pressure flow cell for PPC with transmitter and receiver attached to front and back face shown in Figure 2.
Figure 4. Measurement mode view, and selection of graph scaling parameters.
Figure 5. PPC measurement windows, showing the velocity distributions of the small and big beams. Also shown are the mass distribution and time history of $C_m$ and size distribution parameters, ($D_{10}$, $D_{50}$, and $D_{90}$).

3.0 PPC Measurement Method Theory

The PPC measures the light scattered from individual particles as they traverse a focused beam, Figure 6. The peak intensity and transit time of each traverse is measured, and stored in a histogram. Knowing the peak amplitude and discriminator level, the velocity of each particle can be computed using the formula shown in the figure. The relationship between the measured pulse amplitude and particle size is shown in Figure 8. The basic response function, $F(d,m)$, is the non-dimensional particle scattering cross-section, calculated for a specified light scattering geometry and refractive index, $m$, and is calculated using our code MIEDAT, based on Mie theory.
Figure 6. Schematic layout of general PPC system with light collection in near-forward direction. Particles pass through beam focus and scatter light through lens and into detector.

Figure 7. Pulse measurement for peak amplitude and particle transit time. Only pulses with scattering amplitudes greater than the discriminator level will be validated. Particle velocity is computed by the formula shown, measuring the pulse peak height $A_p$, and the transit time $\Delta t$, and specifying the $1/e^2$ beam diameter $W_0$ and discriminator level, $A_t$. 

$$\text{Velocity} = \left(\frac{W_0}{\Delta t}\right)^2 \cdot \left[0.5 \ln\left(\frac{A_p}{A_t}\right)\right]^{1/2}$$
PSDF Beam geometries, with $\theta = 10.5$ degrees. Big beam ($W_0 = 154$ microns) at $\theta_{in} = 1.75$. Small Beam $\theta_{in}$ at 6.75 degrees.

Amplitude resolution of Small beam equals 0.10. $\lambda = 0.635$ microns.

Figure 8. Non-Dimensional light scattering cross-section $F(d)$ and slope $\frac{d\ln A}{d\ln d}$ as a function of particle size for uniform intensity illumination by a laser. Response functions show relationship between scattering for RS-2 diffraction reticle and opaque particles, along with correction for response “roll-off” when particle becomes large relative to Gaussian laser beam ($d/W_0 > 0.25$).

A near-forward light scattering geometry is chosen (in the range of 1-5 degrees from the beam axis) to minimize scattering sensitivity to the particle refractive index. Figure 9 shows this effect as the absorption component is varied by a factor of 1000 from $m = 1.6 - 1i$ to $m = 1.6 - 0.001i$. The first value corresponds to black carbon, while the second value corresponds to “dirty glass”. For a one hundred-fold decrease there is almost no change in the mean value of the response function for the entire size range, although there are some “resonances” in the size range of 1 – 5 microns. For a broad size distribution, using the mean value of scattering (opaque particles) gives essentially the same data interpretation. For the most transparent case, $(0.001i)$ and even for pure transparent particles, there is little difference in $F(d)$ up to 10 micron particle sizes, with increasing scattering for transparent particles above 10 microns in size. The refractive index is generally proportional to the mass fraction of absorbing vs. transparent materials in the resulting ash. Based on the results of Figure 9, only 1% of black carbon content is required to give an absorption refractive index of 0.01i. It is known that the carbon content of filter collected ash is on the order of 35%. Therefore we conclude that coal-fired ash (generally grey) has a refractive index greater than 1.6 – 0.01i, and thus will scatter light as an opaque material up to 100 microns in size.
Figure 9. Variation of scattering signal response function, $F(d)$ with decreasing values for the absorption component of the refractive index.

The key element of the PPC method is an intensity deconvolution technique which accounts for the fact that the beam intensity seen by any random particle trajectory through the beam is in fact not of a uniform intensity. Thus a large particle passing through the edge of the beam can give the same scattering intensity as a small particle passing through the beam center. The scattering amplitude for a specified light collection geometry is given by:

$$A_p = G \cdot I_p(x,z) \cdot F(d,m) \quad (1)$$

where $G$ is a known gain factor, $I_p(x,z)$ is the local peak intensity of a particle trajectory with random coordinates $(x,z)$ within the sample volume cross-section.

Only particles which pass through a “sample volume” defined by the image of the slit at the detector and the beam focus are observed by the detector. For particles outside the sample volume region, their light is scattered to a point that does not pass through the detector slit. This sample volume typically has the dimensions of $10^{-4}$ to $10^{-6}$ cm$^3$. Figure 10 shows a calculated (MIEDAT) sample volume intensity cross-section map, with the various colors indicating contour levels decreasing by a factor of two from the peak intensity.
Figure 10. Sample volume intensity cross-section contour map calculated using Miedat. The blue lines are the $1/e^2$ contour of the illumination laser beam. Note the axial scale (z-coordinate) is approximately 200 times longer than the radial coordinate, x. The beam waist is $W_0$.

The contour map of 12 can then be used to compute the cross-section probability map of 13, which is normalized on the $1/e^2$ cross section. This gives the fractional probability of a particle passing through any region of the beam, which is valid for sufficiently large statistics, i.e. for more than 10,000 sampled random particle trajectories. Typically the sample volume is on the order of 5-8 mm long by 0.3 mm.
Figure 11. Differential sample volume cross-section, derived from the contour map of Figure 10, showing the fractional probability of number count contributions of each section of the sample volume (corresponding to sample volume intensity J).

It is important to note that the PPC is a single particle scattering instrument, i.e. there can only be one particle at a time passing through the sample volume. This is why the instrument is most suitable for low concentration applications (typically less than 1 g/m³). This condition is achieved when the instantaneous cumulative number concentration $N_{\text{max}}$ is satisfied by the following formula:

$$N_{\text{max}} < \frac{2P_i}{V_{\text{samp}}}$$  \hspace{1cm} (2)

where $P_i$ is the Poisson probability of there being 2 or more particles in the sample volume, and $V_{\text{samp}}$ is the sample volume. If we choose $P_i = 0.2$, i.e. 20% chance of particle overlap, which gives little error on the mass measurement, the maximum number concentration is approximately half the inverse sample volume size. For applications at very low concentrations, this limit is seldom reached, although nearly-instantaneous events in the process can generate relatively high short term concentrations.

Once we have all operational conditions satisfied, we obtain a measurement of the number of particle counts for each scattering amplitude in the form of a count spectrum as shown in 14. From these measurements, along with the particle velocity measurements (which are generally independent of size for uniform turbulent flows in the sample volume), we can compute the size distribution. A simpler form can be derived from these equations, giving a more physical and intuitive relationship between the measured
amplitude spectrum, and the desired result, namely the number frequency \( \frac{dN}{dlnd} \) as follows:

\[
(\frac{dN}{dlnd})_m = -\left[ \frac{(dC/dlnA)_m}{Q (1-E_m)} \right] (\frac{dlnA}{dlnd})_m
\]

where the suffix \( m \) refers to a finite size bin (typically ±5% amplitude resolution) corresponding to a calibrated particle size passing through the peak of the sample volume intensity distribution.

\[
Q = tV_{vel} \Delta S_r = \text{reference gas sample volume, cm}^3
\]

\[
t = \text{measurement sample time, sec.}
\]

\[
V_{vel} = \text{average of all particle velocities through sample volume.}
\]

\[
\Delta S_r = \frac{1}{e^2} \text{sample volume cross-section, cm}^2
\]

\( E_k \) = Correction term computed by the deconvolution algorithm, dependent on the differential cross-section, and measured size distribution. The solution is developed from the largest particle size down to the smallest. Typical values of \( E_k \) range from 0.15 – 0.35, and thus this correction is 2\(^{rd}\) order.

\[
(\frac{dlnA}{dlnd})_m = \ln \text{derivative of the response function } F(d,m), \text{ for a given size, } d, \text{ and the refractive index } m, \text{ see Figures 8,9.}
\]

Figure 22. Measured amplitude count spectrum \( C(A_p) \) as a function of the scattering amplitude \( A_p \) for two different beams in the PPC instrument.

In other words the number frequency is given by the negative of the derivative of the amplitude spectrum, combined with the calculated response function derivative,
dlnA/dlnd. Implicit in equation 3 is the calculated response function, F(d,m), along with one calibration size associated with a specified amplitude bin number. The amplitude spectrum is always referenced to this reference calibration size, correcting for any change in the laser beam intensity relative to the initial calibration value. To derive a stable result for the number frequency, the accuracy is dependent on the total number of particle counts.

We have developed robust local averaging algorithms, which, based on Poisson statistics and the fundamental deconvolution equations, allows us to derive the most accurate number frequency result for a given total number of particle counts. Increased counts always provide an improved result proportional to the square root of the total number of counts in each size bin. Once the number frequency distribution is determined, the results can be readily converted to particle Area or Volume frequencies. In turn, the volume frequency can be converted to a mass frequency by using an appropriate “optical” particle density, which turns out to be the bulk particle density.

Despite the fact that the particles are non-spherical, and generally opaque, we can obtain optical mass measurement results which agree within 15% of independent mass measurements, by essentially adding up the particles one by one to give a total mass measurement. Most importantly, having the complete size distribution allows us to obtain measurements of the total mass, or any sub-component fraction of the mass distribution, e.g. PM-10 or PM-2.5 type measurements. For process operations, the small fraction of large particles are most important for turbine operation, while for environmental exposure, the number count below several microns is of most interest. The PPC allows detailed discrimination of the entire distribution, giving the absolute concentration for each size class.

4.0 Mass Balance Flow Facility (MBFF)

Figure 13 shows overall views of the MBFF at PMC and the figure captions describe the overall layout. The basic seeded flow can range from 150 -600 cfm ±3%, and the mass flow rate can be varied by a factor of 20 from 0.5 to 10 gm/min (±10%) from the AccuRate™ auger feeder. The auger feeder provides quasi-steady mass feed-rates that are measured about every third size distribution result by collecting and weighing approximately 2-4 gms of sample at the auger exit for a period of 4-8 minutes. Specific mass feed-rates could be accurately determined with accuracy better than 5%. This gives mass feed concentrations on the order of 50 mg/m³ up to 1000 mg/m³. PPC software allows both short term and long term continuous integrations on a rolling time basis which allow operators to observe both short term (1 second) count-rate fluctuations, and longer term average size distribution and absolute particle concentration variations.

The MBFF method is simpler, and we believe more accurate than sampling and weighing milligram level samples of powder in the flow (e.g. Method 5). Repeatability on total mass of better than 5% can be achieved over the short term. All instruments are tested with actual dust flows simulating the application environment, and confirm that the PPC instruments are able to quantitatively measure mass flow concentrations (±15%) along with particle size and velocity (±4%).
Figure 13. Overview photo of vertical Mass Balance Flow Facility (MBFF) at PMC. An AccuRate ™ feeder meters dust flow rates ranging from 0.5 – 10 gm/min into a vibrating ramp and venturi eductor. The main flow pipe is 3 inches diameter, and air flow is provided by a variable speed blower to give velocities ranging from 10-60 m/s. In situ measurements are performed in the free jet at this exit. The dust-seeded flow passes through the PPC instrument, exhausting through a fan and filter box.

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