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# A scattering ratio method for sizing particulates in a plasma

**G Praburam† and J Goree**

Department of Physics and Astronomy, The University of Iowa, Iowa City, IA 52242, USA

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**Abstract.** Particulates suspended in plasma can be sized *in situ* using the scattering ratio method, which involves measuring the ratio of the parallel and perpendicular polarizations of light scattered at 90°. This method of plasma monitoring is of interest for controlling contamination of silicon wafers and other thin film products during plasma etching and deposition procedures. For parameters typical of plasma processing, we report Mie scattering computations to test the method's sensitivity to the optical design and to uncertainties in the particle parameters. A ±20% error in the size determination can result either from an uncertainty of ±1 either in the real or in the imaginary part of the refractive index or from a particle shape that deviates significantly from a sphere. A ±5% error results from a 0.1° error in aligning the scattering angle. To measure particulate diameters as small as 0.05 $\mu$m, the detector solid angle should be $< 10^{-5}$ Sr and the extinction ratio of the polarizer must be $< 10^{-4}$. A calculation of the signal-to-noise ratio reveals that it is untenably weak for particle diameters smaller than about 0.04 $\mu$m. The scattering ratio method is usually inapplicable for polydisperse particulates, but it will still work in many cases for many plasma applications, in which particles stratify in different layers according to their size.

## 1. Introduction

Particulate contamination of silicon wafers and other thin film products is a serious and costly problem that occurs when a substrate undergoes etching and deposition steps (Selwyn 1994). Particles either grow in the plasma or are released from vacuum vessel surfaces (Goree and Sheridan 1992). Those that are produced in the plasma have been shown in some experiments to be spherical when they are very small (radius $< 0.05$ $\mu$m) and almost always coagulated when they grow to larger sizes (Praburam and Goree 1995). Once in the plasma, particulates become electrically charged and levitated until they fall onto a surface such as a wafer. Considerable effort has been devoted to identifying the causes of this contamination and designing methods of detecting and avoiding it.

Manufacturers of plasma processing equipment must now deliver products that meet contamination specifications of better than 0.05 particles cm$^{-2}$, for particle sizes $> 0.3$ $\mu$m. The maximum tolerable particulate size is constantly being pushed downward, as features patterned onto silicon wafers become smaller. It will not be long before 0.25 $\mu$m features are common. For manufacturers of plasma-processing equipment, avoiding particles smaller than 0.3 $\mu$m is presently a challenge.

Manufacturers would like to detect particles as small as 0.1 $\mu$m. Doing this *in situ*, rather than after the contamination has been done, is most desirable. Here we will deal with a method that offers promise for meeting these requirements.

The scattering ratio method of measuring particulates is an established technique in aerosol science, and it was recently demonstrated for particles suspended in a radio-frequency plasma by Shiratani and Watanabe (1992). They used a polarized argon laser beam, which was first passed through a depolarizer and then directed along a horizontal axis through the cloud of suspended particles. Using the traditional scattering ratio method, scattered light was collected on a horizontal plane by two detector arms aligned at 90° from the incident light. Polarizers were installed so that the parallel polarization was detected on one arm and the perpendicular polarization on the other. In addition to the polarizers, each arm was fitted with a lens, three apertures to define the solid angle of detection and a photomultiplier tube. By calculating the ratio of the two signals, $\sigma = I_{\parallel}/I_{\perp}$, the experimenters determined the size of the particulates suspended in their experiment. This result can be combined with a separate measurement of the intensity of one of the polarizations to yield the number density.

In this paper, using Mie scattering calculations, we attempt to provide the detailed quantitative information needed by anyone who wishes to use this method to size

† Present address: Applied Materials, Santa Clara, CA, USA.

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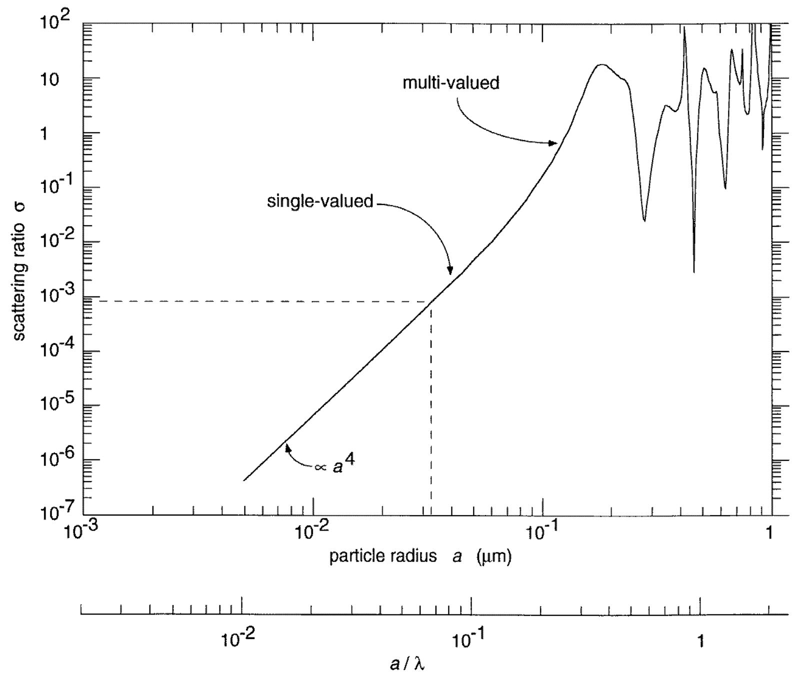


**Figure 1.** Variation of scattering ratio $\sigma$ with particle radius $a$. The scattering ratio $\sigma$ is the ratio of parallel ($I_\parallel$) and perpendicular ($I_\perp$) polarized scattered intensities. The size measurement involves measuring $I_\parallel$ and $I_\perp$ experimentally and then comparing their ratio with the theoretical curve (as shown by the broken lines). Above a radius of 0.1λ, the curve is multi-valued and it is difficult to determine the particle size. Below this limit, the curve is single-valued and $\sigma \propto a^4$. These Mie scattering calculations are for λ = 0.488 $\mu$m and a homogeneous sphere with refractive index $N$ = 2 – i.

the particles suspended in a plasma. We test the sensitivity of the scattering ratio method to particulate parameters including the refractive index, shape and size distribution in the small particle size regime (diameter less than one-fifth the optical wavelength). This is important, because in many cases particles in plasmas are non-spherical, polydisperse, or have an unknown refractive index. We also quantify the errors in size measurements and a limit of the smallest size that can be measured due to optical imperfections. Based on our results, we provide a few suggestions for choosing an acceptable detector solid angle and polarizer extinction ratio. We also compute the signal-to-noise ratio that can be expected and discuss how it restricts the successful use of this method to particulates larger than about 0.02 $\mu$m radius.

## 2. The scattering ratio method

Here we briefly review the scattering ratio method (Sinclair and La Mer 1949). The particle size is determined from the ratio $\sigma = I_\parallel/I_\perp$ of the intensities of the parallel ($I_\parallel$) and the perpendicular ($I_\perp$) polarized components of the scattered light.

For a system of monosize spherical particulates, $I_\parallel$ and $I_\perp$ are functions of only three parameters: relative refractive index $m = N/N_m$, scattering angle $\theta$ and size parameter $x = 2\pi N_m a/\lambda$. Here $N$ and $N_m$ are the refractive indices of the particle and medium, $a$ is the particulate radius and $\lambda$ is the wavelength of incident radiation. The scattering ratio $\sigma$ is also a function of $m$, $\theta$ and $x$. For given values of $m$ and $\theta$, $\sigma$ depends only on the size parameter $x$; hence polarization measurements for a given $m$ and $\theta$ can be used to determine the particle size. After determining the particle size, the number density can be readily computed using Mie scattering theory for either $I_\parallel$ or $I_\perp$.

The particle size is deduced by comparing the measured value of $\sigma$ to a theoretical plot of $\sigma$ versus particulate size. This plot can be prepared using a Mie scattering code for homogeneous spheres, such as the one presented by Bohren and Huffman (1983), which we used for this paper. Figure 1 is a representative plot of $\sigma$ versus $a$ for 90° scattering. This assumes a sphere suspended in a plasma with $N_m = 1$ and illuminated by an argon laser ($\lambda = 0.488$ $\mu$m). The complex refractive index $N = N_r + N_i$ is assumed to be 2.0 − 1.0i, which is typical of carbon in graphite form, although there is an uncertainty of this value (Hodkinson 1964).

In figure 1, note that $\sigma$ is a single-valued monotonic function of $a/\lambda < 0.1$, whereas for larger particle sizes it is multi-valued. For the monotonic region, the scattering ratio scales with particle size according to $\sigma \propto a^4$. It is in this region that straightforward and unambiguous particulate sizing measurements are possible. For larger particles, where $\sigma$ becomes a multi-valued function of $a$, accurate particulate sizing is more complicated, requiring for example combining the $\sigma$-measurement with another light scattering measurement or making $\sigma$ measurements at three different wavelengths (Heller and Tabibian 1962). In this paper, we concentrate on using the method in the monotonic region, $a/\lambda < 0.1$.

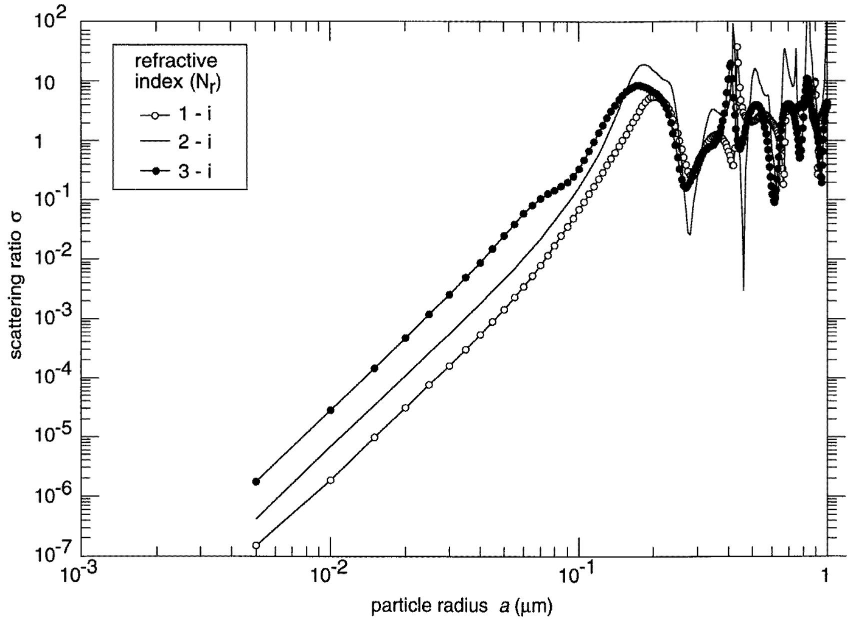


**Figure 2.** The scattering ratio $\sigma$ versus particle radius *a* for various values of the *real* part of the refractive index, $N_r$. The polarization ratio method requires a knowledge of the refractive index.

## 3. Sensitivity to particle parameters

Errors in the size measurement can arise due to several factors. In this section, we quantify the errors introduced by uncertainties in the particulate's refractive index, shape and size dispersion. The sensitivity to optical system parameters is treated in the following section.

### 3.1. Errors due to uncertainties in the refractive index

The particle's refractive index must be known to use this method, but reported values are often unavailable. We have calculated the uncertainty (error bar) in the size measurement due to an uncertainty in the particle's refractive index ($N_r + \mathrm{i}N_i$). To do this, we computed $\sigma$ as a function of particulate radius for various values of $N_r$ and $N_i$, yielding the results shown in figures 2 and 3, respectively. The curves do not coincide, and for this reason an uncertainty in the refractive index causes a corresponding uncertainty in the particle size, for a given measured value of $\sigma$. We used these data to quantify the uncertainties, and the results are shown in figures 4 and 5. For example, figures 4 and 5 show that an error in the size measurement can be $\pm 20\%$ or more, for an uncertainty of $\pm 1$ in $N_r$ or $N_i$. The error increases for smaller particulates.

**3.1.1. Errors due to the uncertainties in the shape.** Particles grown in plasmas are at least in some cases spheroidal for radius $< 0.05$ $\mu$m, and tend to be string-like conglomerates for larger sizes (Praburam and Goree 1995). For this reason, the particle shape is a concern in interpreting data only for sizes $a \geq 0.05$ $\mu$m.

To test the scattering ratio method's sensitivity to particle shape, we compared the two extreme cases of spherical and infinite cylinder particles. The same values of $N$ and $\lambda$ were assumed in both cases. We used the code presented by Bohren and Huffman (1983), which assumes an infinite right circular cylinder illuminated normal to the cylinder's axis.

This comparison of the scattering ratio $\sigma$ for cylinders and spheres is shown in figure 6. The curves reveal a discrepancy in the size determination from a given value of $\sigma$, depending on the particle's shape. The average error is $+20\%$ for $a < 0.05$ $\mu$m.

**3.1.2. Errors due to a polydisperse size distribution.** Size dispersion is usually a concern in using Mie scattering to size the particles in a cloud. However, it is not always a critical problem for particles grown in a plasma. In at least some cases that have been reported, particles have been shown to stratify in layers in a plasma according to their size. This is because the height at which they are electrically levitated depends on their charge-to-mass ratio, which is a function of size. Thus, even though the size dispersion is usually at least 10% when integrated over the entire plasma volume, the size dispersion is less in a given layer (Praburam and Goree 1994). If the diameters of all particles in a polydisperse system do not differ by more than 10%, the results will approximate an average value (Orr and Dallavalle 1954). When there is a greater disparity, the light scattering from larger particles predominates.

## 4. Sensitivity to optics

### 4.1. Signal-to-noise ratio

Achieving a detectable signal strength is an important consideration in designing the optics. Here we illustrate how to estimate the signal-to-noise ratio and show how it depends critically on the particle size.

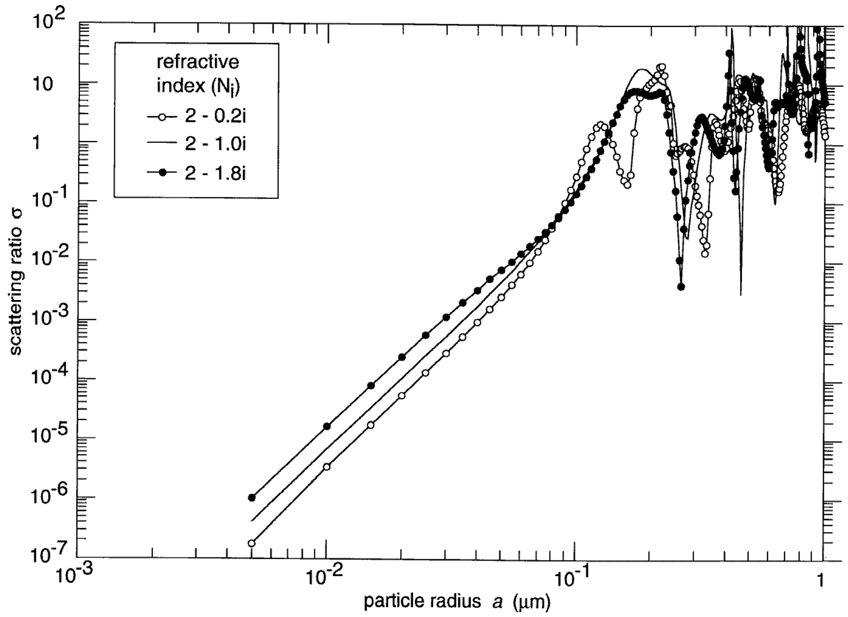


**Figure 3.** The scattering ratio as in figure 2, but for various values of the *imaginary* part of the refractive index, $N_i$.

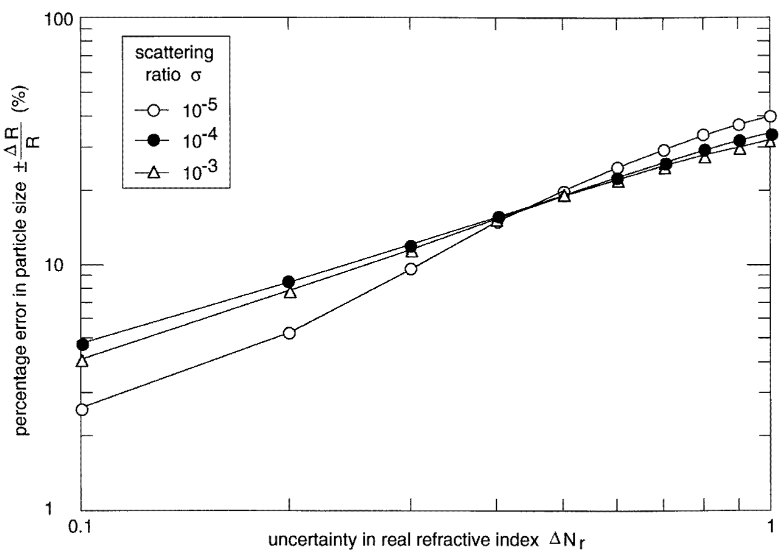


**Figure 4.** The uncertainty (error bar) in particle size due to an uncertainty in the *real* part of the refractive index, $N_r$, for various scattering ratios $\sigma$. Recall that $\sigma$ corresponds to the particle size *a*. The percentage uncertainty (error) was computed using data as shown in figure 2. The error increases with uncertainty in $N_r$ and for smaller particles (smaller $\sigma$).

The signal is determined by the number of photons collected and the detection efficiency. The number of photons scattered per unit time into a solid angle $\Delta\Omega$ is $N = \Gamma(\mathrm{d}\sigma/\mathrm{d}\omega)n\Delta\Omega\Delta V$, where $\Gamma$ is the flux of incident photons, $\mathrm{d}\sigma/\mathrm{d}\omega$ is the differential scattering cross section, $n$ is the number density of the scatterers and $\Delta V$ is the scattering volume. Typical values for the signal strength $N$ for parallel and perpendicular polarizations are $N_\parallel = 1.45 \times 10^4\ \mathrm{s}^{-1}$ and $N_\perp = 3.10 \times 10^6\ \mathrm{s}^{-1}$, where we have used the following parameters: particle size and density $a = 0.05\ \mu$m and $n = 10^{13}\ \mathrm{m}^{-3}$, laser power and wavelength $P = 0.5$ W and $\lambda = 0.5\ \mu$m, solid angle of the detector $\Omega = 10^{-5}$ Sr, polarizer transmission 35% and interference filter transmission 50%.

In a simple current-measurement detection scheme, the signal-to-noise ratio (SNR) at the detector can be very weak for small particles. For example, for a photomultiplier tube with a quantum efficiency of 15% and a typical dark current noise (we assume an EMI 9659QB with an S20B photocathode), we computed $\mathrm{SNR}_\parallel = 0.17$ and $\mathrm{SNR}_\perp = 37.7$. $\mathrm{SNR}_\parallel$ is less than unity, which is untenably weak.

The SNR can be improved by using either a lock-in amplifier or photon detection and by cooling the photomultiplier tube. A lock-in amplifier improves the SNR

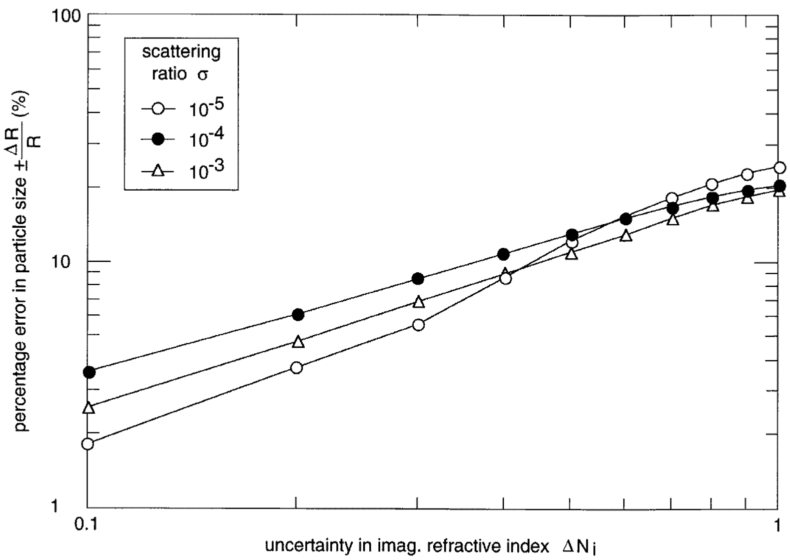


**Figure 5.** The uncertainty (error bar) as in figure 4, but due to an uncertainty in the *imaginary* part of the refractive index, $N_i$. These results were computed using data as shown in figure 3.

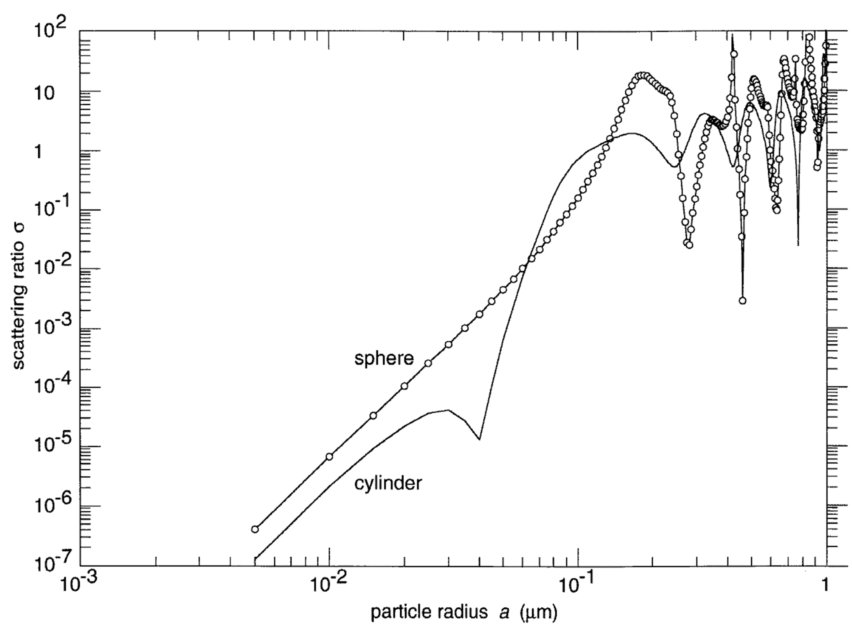


**Figure 6.** The scattering ratio $\sigma$ versus particle radius for a sphere and an infinite cylinder of the same radius. The poor agreement between the curves shows that the sizing method yields an imprecise result if the particle shape is unknown. The wavelength and the particle refractive index are the same as in figure 1.

by a factor $(\tau f)^{1/2}$, where $\tau$ is an integration time and $f$ is a chopping frequency (Goree 1985). This factor is typically an improvement of about $10^2$. Cooling the photomultiplier tube will eliminate dark current noise and further increase the SNR. For the 0.05 $\mu$m radius particles assumed above, this would yield a satisfactory $\mathrm{SNR}_{\parallel} > 1$. With the dark current eliminated, the chief source of noise would be counting statistics, due to the finite number of photons detected during the measurement interval. Photon counting detection would be more useful than lock-in detection in this case. For a 0.1 s interval, it would yield a sufficient $\mathrm{SNR}_{\parallel} = 17$ for a particle size of $a = 0.05$ $\mu$m. The SNR could be further improved by enlarging the solid angle of detection, although this is unattractive because it involves a trade-off with achieving a desired size resolution, as discussed below.

Any attempt to improve the SNR will ultimately be defeated at a small particulate size. The SNR improvement that can be achieved with lock-in or photon-counting detection is two or three decades, which is cancelled by reducing the particle size merely by a factor of two. This is due to the strong scaling of the scattering intensity with particle size, $I_{\parallel} \propto a^{10}$ and $I_{\perp} \propto a^{6}$. We conclude that the method is restricted to particulates larger than about

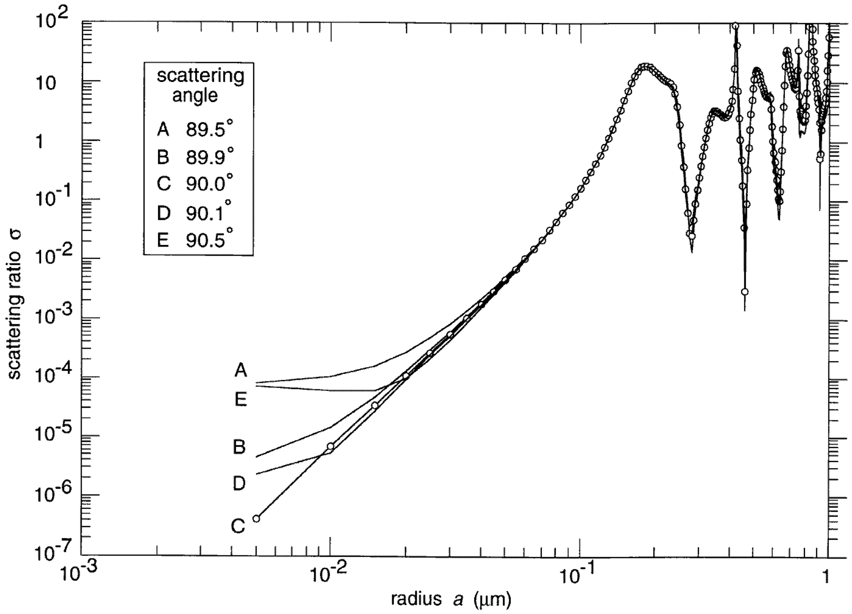


**Figure 7.** The scattering ratio versus particle radius $a$, for various scattering angles. A series of curves corresponding to various scattering angles indicates errors in the size measurement due to misalignment of the 90° scattering angle.

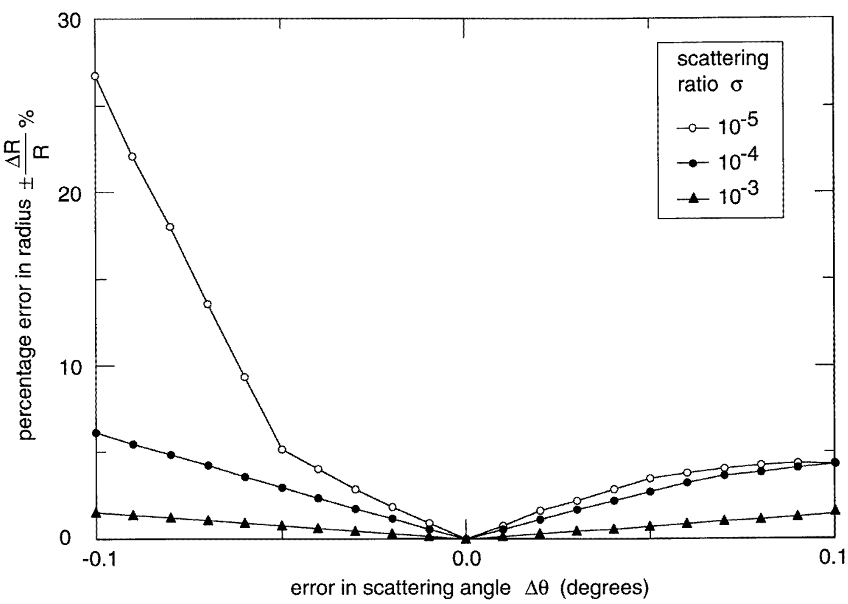


**Figure 8.** The percentage error in particle radius due to misalignment of the 90° scattering angle, for various scattering ratios $\sigma$. Note that the scattering ratio corresponds to particle size. These results were computed based on data like those shown in figure 7. The error in particle size increases with the error in scattering angle and for smaller particles (smaller $\sigma$).

0.02 $\mu$m radius. The exact value of the lower limit on the detectable size depends on the details of the particular experiment.

When the scattering ratio method is used under atmospheric conditions, scattering by molecular gas is an additional source of noise. However, for plasma conditions with a gas pressure of typically 1 mbar, this is not a significant problem. Scattering by imperfections in the windows of the vacuum vessel is likely to be a more significant source of noise.

### 4.2. Design considerations

In practice, the optical set-up is not ideal. The scattering angle is not perfectly 90° and the polarizers do not fully reject light of the wrong polarization. These imperfections affect the measured value of $\sigma$ and this deserves careful attention because the strong scaling $\sigma \propto a^4$ means that a small error in $\sigma$ value results in a significant error in $a$. Using the same Mie scattering code as before, we analysed these effects.

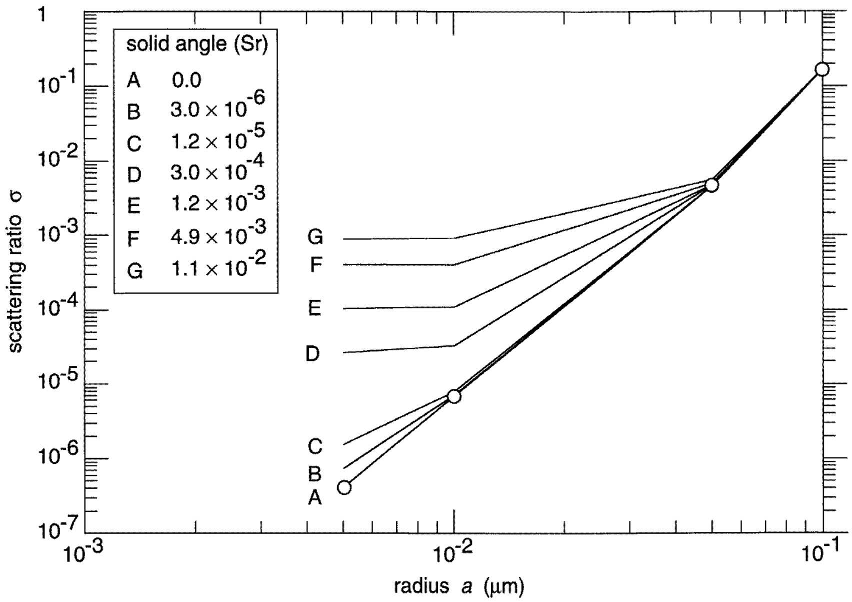


**Figure 9.** The scattering ratio versus particle radius, for various solid angles of the detector. The uncertainty in size increases with the solid angle. For $a < 0.05$ $\mu$m, the solid angle should be less than $10^{-5}$ Sr to obtain a sufficiently pure 90° signal.

**4.2.1. Scattering angle.** The scattering angle for this method is chosen to be 90°, because it yields the greatest difference between the two scattered intensities $I_{\parallel}$ and $I_{\perp}$. However, a small error in aligning the scattering angle at 90° can introduce a significant error in the size measurement. This happens because, at angles other than 90°, there is finite electric dipole scattering into the parallel polarization, which one wishes to avoid.

To quantify the measurement error due to a misaligned scattering angle, we computed $\sigma$ as a function of $a$ for various scattering angles $\theta$, ranging from 89.5° to 90.5° (corresponding to a maximum ±0.5° misalignment). Based on curves like those shown in figure 7, we computed the percentage error in $a$ as a function of the angular error $\Delta\theta$ for various $\sigma$ (corresponding to particle radius) and the results are shown in figure 8. It is evident from figure 8 that the error in $a$ increases with the error $\Delta\theta$ and also increases for smaller particulates. An error in size measurement can be ±5% for $a < 0.05$ $\mu$m and −20% or more for $a < 0.01$ $\mu$m, for an error of 0.1° in the scattering angle. The precision of the optical components should be selected depending on the accuracy of size that one needs and how small the particles are.

**4.2.2. Apertures.** The detector's solid angle limits both the smallest size that can be measured and the accuracy of the particle size measurement. It is possible to choose a very small solid angle to collect almost pure 90° scattered signal, but this can result in a signal weaker than the noise level. Thus there is a trade-off between the SNR and accuracy in sizing.

To estimate the uncertainty in the size measurement due to a finite angle $\Omega$, we computed the scattering ratio $\sigma$ for various values of $\Omega$, yielding the results shown in figure 9. These curves reveal an uncertainty in the size measurement. Also, it is evident from the curves that $\Omega$ limits the smallest size that can be measured. For example, $\Omega = 10^{-2}$ limits the smallest radius to 0.01 $\mu$m because there is no change in $\sigma$ for $a < 0.01$ $\mu$m. Also, there is a large uncertainty for particulates $a < 0.05$ $\mu$m. The results suggest that, for $a < 0.05$ $\mu$m, $\Omega$ must be reduced to $10^{-5}$.

Divergence in the incident beam can also introduce an error in the size measurement due to introducing a finite range of scattering angles. The principle here is much the same as for the finite detection solid angle, as discussed above. Based on the calculations for the error due to scattering angle errors reported above, we can see that a divergence of 0.5 mrad (0.028°), which is typical for an argon laser, will introduce a non-negligible error in the size measurement, especially for particules with radius smaller than about 0.05 $\mu$m. To eliminate this problem, the beam can be focused to a waist located at the centre of the scattering region. At the focus the wavefronts are nearly non-diverging for a distance called the Rayleigh range. The optics can be configured so that the Rayleigh length is longer than the length of the beam that is viewed by the detection optics.

**4.2.3. Polarizer extinction ratio.** Since this method involves detecting parallel and perpendicular polarized light, it is important to evaluate the quality of the polarizers that are to be used. The extinction ratio of the polarizer (ER) is the ratio of the power transmitted by a polarizer when it is aligned with a polarized light source compared to when it is rotated by 90°. For an ideal polarizer ER = 0, but in practice ER is small and finite. There are two sources of errors from the polarizers which contribute in measuring scattered intensity: the finite ER and a misalignment in $\phi$. The particle size resolution involves a trade-off with the cost of the polarizers. Polarizers with the range ER = $10^{-2}$–$10^{-7}$ are commercially available.

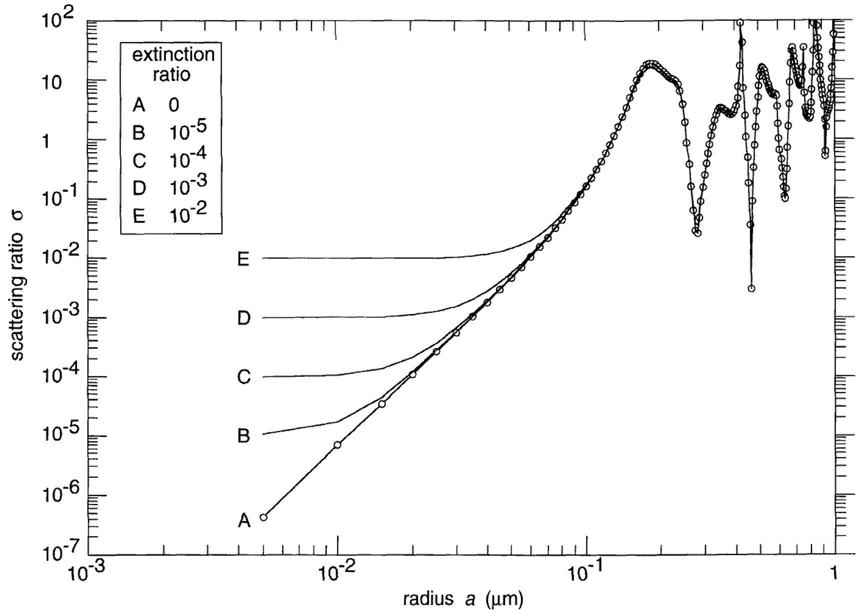


**Figure 10.** The scattering ratio versus particle radius, for various polarizer extinction ratios. A finite extinction ratio limits the size resolution. For $a < 0.05$ $\mu$m, the polarizer extinction ratio should be smaller than $10^{-5}$.

We carried out numerical computations as before to quantify the error in the size measurement due to a finite polarizer ER. Figure 10 is a series of plots of $\sigma$ versus $a$ corresponding to various ERs. It shows that a larger ER leads both to a larger uncertainty in the size measurement and to a higher limit on the smallest particulate size that can be measured. Consider for example curve E in figure 10, corresponding to $\mathrm{ER} = 10^{-2}$. The scattering ratio is almost independent of particle size for $a < 0.05$ $\mu$m, thus the particulate radius cannot be determined in this region. The measurement uncertainties are improved by using a smaller ER. Our results indicate that $\mathrm{ER} < 10^{-4}$ and $\mathrm{ER} < 10^{-5}$ are necessary for $a < 0.05$ $\mu$m and $a < 0.01$ $\mu$m, respectively.

Errors may also be introduced by the misalignment of the polarizer rotation. In practice, the experimenter will rotate the polarizers to attain maximum and minimum signal for small particles, thereby orienting them in the $\parallel$ and $\perp$ directions, respectively. This requires high-precision polarizer mounts. A good polarizer with an ER of $10^{-5}$ will be wasted if it cannot be rotated with a resolution of $10^{-5}$ radius. The most critical adjustment is for the parallel polarization.

## 5. Summary

Practical limitations of sizing particles suspended in a plasma using the scattering ratio method have been evaluated quantitatively. We calculated the error bars in the size measurements due to uncertainties in particulate parameters, such as the particle refractive index and shape. It is found that there can be more than $\pm 20\%$ error for an uncertainty of $\pm 1$ either in the real or in the imaginary part of the refractive index. Another average error of $+20\%$ arises if the particulate shape deviates significantly from a sphere. The method is also useful for polydisperse particles in plasmas, because the particulates are stratified by size when they are suspended.

We also estimated the errors in the size measurement due to imperfections in optics, such as the scattering angle, detector solid angle and polarizer extinction ratio. It is found that, for an error of $0.1^\circ$ in the scattering angle, the error in size can be up to $\pm 5\%$ for $a < 0.05$ $\mu$m and more than $-20\%$ for $a < 0.01$ $\mu$m. A finite detector solid angle and a finite polarizer extinction ratio both yield an uncertainty in the size measurement. They also limit the size resolution. For $a < 0.05$ $\mu$m, the detector solid angle must be reduced to $10^{-5}$ Sr and the polarizer extinction ratio must be smaller than $10^{-4}$.

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